

STUDIES ON EQUILIBRIUM POLYMERIZATION OF CAPROLACTAM

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By
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CERTIFICATE

This is to certify that the present work 'STUDIES ON EQUILIBRIUM POLYMERIZATION OF CAPROLACTAM' has been carried out under my supervision and that this has not been submitted elsewhere for a degree.

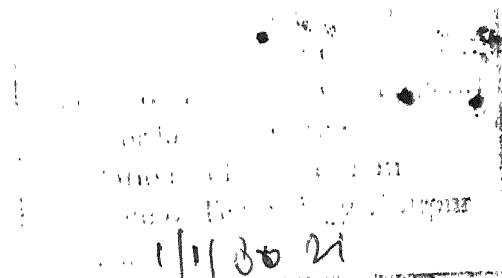
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NOMENCLATURE

B_t	Binomial coefficient
C	Concentration of acid end groups
F	Output rate from the CSTR
F_i	Feed rate to the CSTR
F_v	Rate of evaporation of water from the CSTR
$G(x)$	Normalized distribution function
\bar{G}_x^k	Moments of the normalized distribution
k	kth moment of the distribution
k_1	Rate constant for the ring opening reaction
k_2	Rate constant for the poly condensation reaction
k_3	Rate constant for the poly addition reaction
K_1	Equilibrium constant for the ring opening reaction
K_2	Equilibrium constant for the poly condensation reaction
K_3	Equilibrium constant for the poly addition reaction
M	Concentration of caprolactam
$M(v)$	Original distribution function
\bar{M}_v^k	Moments of the original distribution
S_1	Concentration of the linear monomer
S_2	Concentration of the linear dimer
S_n, S_n	Concentration of the linear m-mer, n-mer
t	Time
T_0	Temperature at the top portion of the CSTR

v	Chain length variable
V	Volume of the CSTR
W	Concentration of water
Z	Concentration of amide group
Γ	Gamma function
ρ	Density of the polymer mixture
τ	Residence time in the CSTR

ABSTRACT

Several reactor models have been cited in literature for carrying out the polymerization of caprolactam into nylon 6. These vary from the simple model of batch reactor to the complex system of a series of continuous stirred tank reactors followed finally by a plug flow reactor. In the present study, the reactor has been modelled by assuming that the top portion of the reactor behaves like a stirred tank reactor and the rest of the reactor as a plug flow reactor. Part of the water fed to the reactor has been assumed to evaporate immediately. The usually made assumption of a correlation between the concentrations of the linear dimer and linear monomer has been eliminated. The modelling equations have been solved using the moment approach. Properties of the polymer product such as the weight-average molecular weight, poly dispersity index and melt viscosity, which were not obtained so far, have been evaluated. The validity of the model in the case of the plug flow reactor has been checked by comparing some of the results with the experimental data that have been published in the literature.

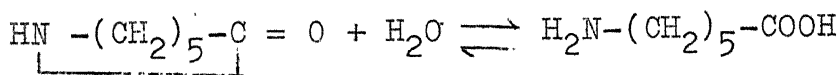
CHAPTER 1

INTRODUCTION

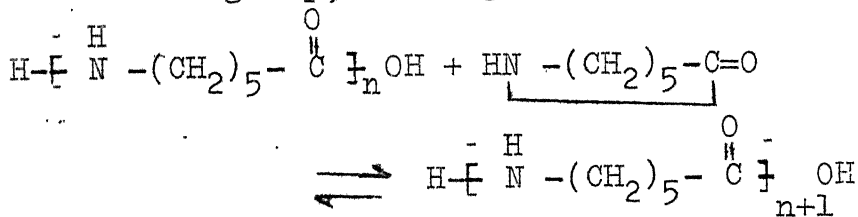
Nylon 6, obtained by the polymerization of caprolactam, has developed into a polymeric substance of significant commercial importance. Caprolactam can be polymerized in three ways: (1) hydrolytic, (2) anionic and (3) cationic. Of the three, hydrolytic polymerization is the one that has been widely followed for the commercial production of Nylon 6.

Hydrolytic polymerization consists of polymerizing caprolactam in the presence of water. Stabilizers or catalysts (usually organic acids) and delustering agents are also added. The broad steps of the reaction mechanism are as follows:

1. Ring Opening: Caprolactam combines with water to form amino caproic acid, which is the linear monomer.

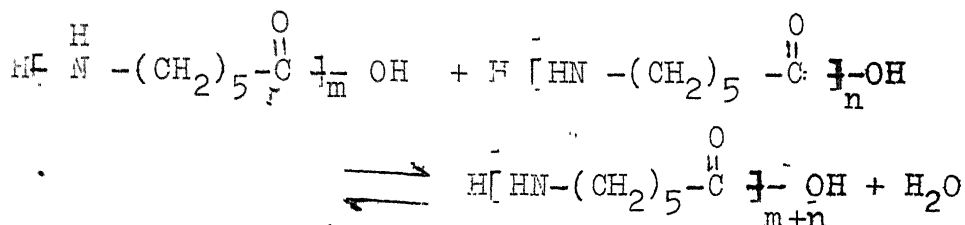


2. Poly-addition: Caprolactam can then successively add onto the acid end-group, forming linear polymer chains.

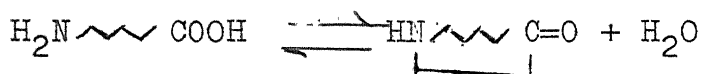


3. Poly-condensation: Two such chains formed by poly-addition can then react with each other, resulting in the

formation of an amide linkage and a molecule of water.



All the three reactions are reversible. If monobasic organic acids are used, they can act as chain length regulators also, since they can react with amino end groups. In addition to these three main reactions, side reactions leading to the formation of cyclic oligomers can also take place.



Of the three main reactions, ring-opening and poly-addition are the reactions by which conversion of caprolactam into the polymer takes place and the poly condensation is the reaction which determines the final degree of polymerization.

Once the desired degree of polymerization is achieved, any monomer present in the polymer mixture, along with cyclic oligomers, is removed either by hot water extraction or by applying vacuum. One of the important factors in the process is the amount of water fed to the reactor. Large amounts of water remaining in the system aid in the reversible reaction of the polymer molecule splitting up into smaller units through the condensation reaction. Thus water must be present in large quantities initially, but must be removed from the

system, once a reasonable degree of conversion of lactam has taken place. The optimal conversion at which water must be removed can therefore be determined only when a good model of the reactor is available. The focus of the present work is to develop a mathematical model of the polymerization reactors.

Both continuous and batch reactors are used industrially. In the case of the continuous reactor, caprolactam and water are admitted at the top of the reactor continuously. The upper part of the reactor is normally at about 200°C . The reaction mass passes then into the lower region of the reactor, which is heated to 260°C . During the passage through this zone, water in the reactor mixture starts boiling and some of the water is removed in the vapour form through the top of the reactor. The reaction mass then enters a second reactor (consisting of two concentric tubes) at the bottom of the outer tube and rises up this tube. During this upward movement, both residual water and that formed by poly condensation can escape more easily. The rising water vapour bubbles generally cause mixing in the reactor. At the top, the polymer melt flows into the inner tube, thereby forming a thin liquor film from which any remaining water easily vaporizes. In this part of the reactor, boiling does not occur.

In the case of the batch reactor, the reaction is carried

normally in two stages. In the first stage, during which ring opening and poly addition reactions occur, the system is kept under elevated pressures (about 4 atms). After the desired degree of conversion of lactam has been reached, vacuum is applied to the reactor, thus removing water. After a definite time, vacuum is broken and the polymer melt is extruded under pressure.

CHAPTER 2

LITERATURE SURVEY

Polymerization of caprolactam, for the commercial production of nylon 6, was first started in Germany in 1940. The initial attempts to understand the kinetics of the polymerization were made simultaneously by Hermans et al. [1] and Kruissink et al. [2] in Netherlands and by Wiloth [3] in Germany. While Kruissink et al. [2] studied the polymerization initiated by amino caproic acid, Hermans et al. [1] investigated the polymerization in the presence of water. They concluded beyond doubt that the polymerization process occurred through the three basic steps (described earlier), a view which was supported by Wiloth [3].^a

Hermans et al. [1] conducted batch experiments at 221.5°C for three different initial compositions of water and caprolactam in the feed, and at 254.5°C for one of the three compositions. Kruissink et al. [2] who did similar experiments, and Hermans et al. [1] concluded that all the three reactions were catalyzed by the acid end groups of polymer chains. The rate constants, according to these groups of workers therefore consisted of two parts, one being for the uncatalyzed reaction and the other for the reactions catalyzed by the acid end groups. The general form of the rate constants was given as

^aThe article by Wiloth is in German, hence his results which are reported here are from English sources where this article has been referred to.

$k_1 = k_1' + k_1'' C$, where the k_1' and k_1'' refer to the uncatalyzed and catalyzed parts respectively and C refers to the concentration of the acid end groups. Numerical values for the k_1' s and k_1'' s as well as for the equilibrium constants at 221.5°C were given by Hermans et al. [1]. In their work, Hermans et al. [1] assumed that the formation of cyclic oligomers was low and that their effect on the kinetics was negligible. They also assumed that the concentration of the linear dimer was equal to that of the linear monomer.

Kinetic data have also been published by Hoftyzer et al. [5]. They used a similar general form for the reaction rate constants and gave numerical values for the rate constants as well as equilibrium constants, for a temperature of 260°C .

Reimschuessel et al. [6] carried out the kinetic studies in the range of 220 – 265°C and determined the temperature dependence of the rate constants. The temperature dependence was correlated by the usual Arrhenius relationship. They have given the values for the activation energy and the pre-exponential factor, for each of the rate constants.

Among the three sets of rate constants that have been given in the literature, the ones estimated by Hermans et al. [1] and those by Reimschuessel et al. [6] conform with each other. so far as the ring-opening and poly addition reactions are concerned. Reimschuessel et al. [6] have expressed the equilibrium constants in terms of the heat of reaction and

entropy change. These values approximate well with those given by Hermans et al. [1]. The various sets of rate constants and equilibrium constants as obtained by the different groups of workers have been given in Table I. Here, it is pertinent to mention the work of Gerdes et al. [7].

Gerdes et al. [7] determined the rate constants for the three basic reactions from the experimental results of Hermans et al. [1] by a parameter estimation technique. The numerical values for the rate constants have not been given. However, they appear to claim that the values given by Hermans et al. [1] are incorrect and that based on the correct values, which were not given, considerable improvement in an existing process was noticed. In describing the kinetics of the process, they have assumed that the concentrations of the linear dimer and the linear monomer are related according to the chain length distribution of Flory [4]. However, it is to be noted that Flory's distribution is valid only for irreversible condensation polymerization.

All the workers mentioned so far neglected the effect of cyclic oligomer formation on the kinetics of the system. Mochizuki and Ito [8] studied the kinetics of the termination reaction (i.e. the reaction of an organic acid, usually added as a stabilizer, with the amino end groups of the polymer chain) and also the formation of the cyclic oligomers. Data, and equilibrium constants and activation energies for these

two reactions have been given [8]. The oligomer content at various times during the course of polymerization was studied. According to their results [8], the concentration of the overall cyclic oligomers is never greater than 2 per cent.

Work on the modelling of nylon 6 reactors was first started by Hoftyzer et al. [5]. Their aim was to optimize the course of temperature and water content in such a way that a certain \overline{DP} (degree of polymerization) was obtained in the minimum possible time. To simplify matters, they presumed that there were no operational limitations for realizing the existence of such an optimal course of temperature and water content for the polymerization process. They also assumed batch operation (or ideal plug flow). By employing dynamic programming, they concluded that the process should be carried out in two stages: the first one operating at a high water content to facilitate the conversion of caprolactam and the second one at a low water content to attain the maximum \overline{DP} through the condensation reaction. In between the two stages water should be removed as rapidly as possible. Two limiting values were assumed for the temperature: the upper limit being the boiling point of lactam at atmospheric pressure and the lower one corresponding to the melting point of the polymer. A degree of polymerization of 140 was reached by this method in the minimal possible time. One of the drawbacks of this model is that it is rather difficult to

realize the instantaneous removal of water present in the system after the first stage, though there are processes which operate on the basic principles upon which this study was based. Yet another drawback is that distribution gets narrowed down.

Nagasubramanian and Reimschuessel [9] analyzed the modelling of reactors for the polymerization process. They devised a system of a series of perfectly mixed stirred tanks followed by a plug flow reactor. In order to obtain the highest possible rates of conversion, they assumed that the reactor system consisting of the stirred tanks 1 to $(N-1)$ was essentially a closed system. Removal of water was done only in the N th reactor, and that too at a finite rate instead of the instantaneous removal as was done by Hoftyzer et al. [5]. This rate was determined from an equation connecting the water concentration and chain length concentration in the N th reactor. They [9] analysed a system consisting of three stirred tank reactors in series, followed by a plug flow reactor. They found that in such a system, considerable reduction in the overall reaction time could be obtained, over the plug flow reactor in which water is removed instantaneously, for attaining the same degree of polymerization. Such a reactor model would be efficient only when three or more stirred tank reactors in series are considered. When only one or two stirred tanks are used in series, the situation would be

different. Moreover, they [9] also have assumed that the concentrations of the linear dimer and linear monomer are equal.

Jacobs and Schweigman [10] have made a detailed study of the modelling of the reactors for the polymerization process. In their model of the reactor, they have considered the reactor to consist of two parts, the first one approximating a stirred tank reactor due to the strong mixing effect caused by bubbling of water vapor and the second part behaving like a plug flow reactor, which is also reasonable because of the high viscosity of the polymer at this stage and the presence of baffles in this part of the reactor. While formulating their mathematical model, they have based their expression for the linear dimer on Flory's distribution, i.e., the same that has been adopted by Gorder et al. [7]. Jacobs and Schweigman [10] determined the effect of water on the \overline{DP} at various temperatures. From their results it is quite evident that even a slight variation in the water content in the reaction mixture can have a great influence on the \overline{DP} . They measured the water content in the reaction mixture based on vapour flow rate measurements and viscosity measurements for various temperatures. On the basis of the results thus obtained, they gave an empirical relationship for the determination of weight fraction of water in the melt at the top of the reactor, as a function of temperature. They considered the extent to

which water should be removed before poly condensation reaction took effect. They concluded that the increase in the relative viscosity was higher the greater being the per cent removal of water from the system. Polymerization at elevated pressures with intermediate water removal has also been considered by them. They found that a 66 per cent decrease in the reaction time could be achieved using this method over the conventional VK (vertical tube) column reactor, but at the expense of simplicity in the reactor design.

Considering the various reactor models so far seen, it is evident a reactor based on plug flow assumption alone would not be an adequate one. Also, having several stirred tank reactors in series without water removal is unrealistic, though physical conditions dictate a combination of stirred tank reactors and plug flow reactor. Hence for simplicity, the model envisaged by Jacobs and Schweigman [10] seems plausible. This model has been adopted in the present study.

The present study aims at calculating properties that have not been calculated hitherto. Of all the workers referred to, Jacobs and Schweigman [10] have calculated the viscosity of a 1 per cent solution of nylon 6 in formic acid. In the present study the melt viscosity, based on the weight-average molecular weight is calculated. Also, all the workers

so far have assumed that the concentrations of the linear dimer and linear monomer are equal or related to each other by Flory's distribution. The present work has attempted to eliminate this assumption.

TABLE 1: VALUES OF THE EQUILIBRIUM CONSTANTS (CALCULATED AND MEASURED)
GIVEN IN LITERATURE

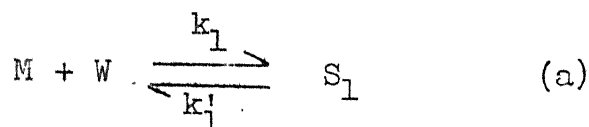
Reference	Type of constants	Reactions	
		Ring Opening	Carbonation
Hermans et al. [1]	Reaction rate (at 221.50°C)	.0008 + 0.17C	1.0 + 21.0C
	Equilibrium (at 221.50°C)	400	1/720
Kruissink et al. [2]	Equilibrium (at 221.50°C)	382	1/425
Reimschuessel et al. [6]	Reaction rate (at 221.50°C)	0.00085 + 0.211C	0.937 + 17.01C
	Equilibrium (at 221.50°C)	451	1/326
	Reaction rate (at 260°C)	0.004 + 0.838C	4.92 + 77.8C
	Equilibrium (at 260°C)	386.5	1/526.5
Hoflyzer et al. [5]	Reaction rate (at 260°C)	0.004 + 0.82C	4.9 + 79.0C
	Equilibrium (at 260°C)	344.9	1/470

CHAPTER 3

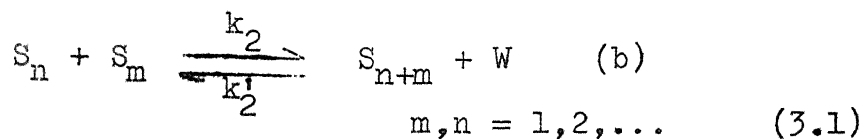
FORMULATION OF MODELLING EQUATIONS

As stated in Chapter 1, during the polymerization of caprolactam to nylon 6 three basic reactions have been recognized. They are:

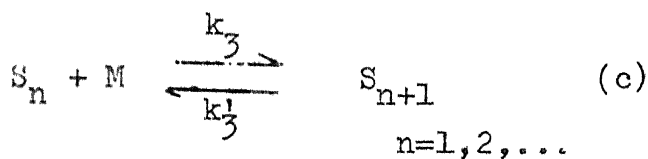
(1) Ring Opening:



(2) Poly Condensation:



(3) Poly Addition:



For the symbols used, reference is made to the list of symbols.

Equations for a Plug Flow Reactor or a Batch Reactor:

From the above three reactions, rate equations for the concentration of caprolactam, acid and groups, amide groups and amino caproic acid are given [1] as

$$\frac{dM}{dt} = -k_1(MW - K_1 S_1) - k_3(MC - K_3(C - S_1)) \quad (a)$$

$$\frac{dC}{dt} = k_1(MW - K_1 S_1) - k_2(C^2 - K_2 WZ) \quad (b)$$

$$\frac{dZ}{dt} = k_2(C^2 - K_2 WZ) + k_3(MC - K_3(C - S_1)) \quad (c)$$

$$\begin{aligned} \frac{dS_1}{dt} = & k_1(MW - K_1 S_1) - 2k_2(CS_1 - K_2 W(C - S_1)) \\ & - k_3(MS_1 - K_3 S_2) \end{aligned} \quad (d)$$

In the last equation (i.e. 3.2 d), 'S₂' refers to the concentration of the linear dimer. This equation explains as to why a relationship between S₂ and S₁ had to be assumed by the previous workers. To avoid this difficulty and to find the weight-average molecular weight \bar{M}_w , the concentrations of all S_n are needed. The rate expressions for the concentration of S_n can be written as

$$\frac{dS_n}{dt} = -k_1(MW - K_1 S_1) - k_3(M \sum_{n=1}^{\infty} S_n - K_3 \sum_{n=1}^{\infty} S_{n+1}) \quad (a)$$

$$\begin{aligned} \frac{dS_1}{dt} = & k_1(MW - K_1 S_1) - 2k_2(S_1 \sum_{m=1}^{\infty} S_m - K_2 W \sum_{m=1}^{\infty} S_{m+1}) \\ & - k_3(MS_1 - K_3 S_2) \end{aligned} \quad (b)$$

$$\begin{aligned} \frac{dS_n}{dt} = & k_2 \sum_{m=1}^{n-1} S_m S_{n-m} + 2k_2 K_2 W \sum_{m=n+1}^{\infty} S_m - 2k_2 S_n \sum_{m=1}^{\infty} S_m \\ & - k_2 K_2 W S_n (n-1) + k_3 M (S_{n+1} - S_n) + k_3 K_3 (S_{n+1} - S_n) \end{aligned} \quad (c)$$

$n \geq 2$

In deriving the last equation in (3.3), it has been assumed that all the $(n-1)$ amide bonds that are present in a polymer chain of n units, are equally accessible, for the reverse reaction.

'C' the concentration of the acid end groups is nothing but the sum total of the concentrations of all the linear chains. Hence 'C' can be denoted by

$$C = \sum_{n=1}^{\infty} S_n \quad (3.4)$$

$$\frac{dC}{dt} = \sum_{n=1}^{\infty} \frac{dS_n}{dt} \quad (3.5)$$

If (3.3(b),(c)) are substituted into the above, eqn.(3.2) (b) is recovered. Now

$$Z = \sum_{n=1}^{\infty} (n-1) S_n \quad (3.6)$$

and therefore,

$$\frac{dZ}{dt} = \sum_{n=1}^{\infty} \frac{d}{dt} ((n-1)S_n) \quad (3.7)$$

To obtain the expression on the right-hand side of eqn.(3.7), each term on the right-hand side of eqn.(3.4(c)) has to be multiplied by $(n-1)$ and the resulting expressions then summed up. When this is done, eqn.(3.2(b)) is obtained. These results prove the consistency of the present model with the previous rate expressions. It might be pointed out that,

in general, integration of the equation for S_n requires S_{n+1} . Thus integration of successive equations, which is possible for irreversible polymerizations, can not be carried out here.

The three equations of (3.3) are now made use of to derive the moment equations. The need for the moment equations will be given in the next chapter.

In general, the k th moment λ_k is defined as,

$$\lambda_k = \sum_{n=1}^{\infty} n^k S_n \quad (3.8)$$

To get the k th moment, the expression on the right-hand side of equation (3.3(c)) is multiplied by n^k and then summed up from $n=2$ to $n=\infty$. This is then added to eqn.(3.3(b)). The result is

$$\begin{aligned} \frac{d\lambda_k}{dt} = & k_1(MW - K_1 S_1) - 2k_2(CS_1 - K_2 W(C - S_1)) - k_3(MS_1 - k_3 S_2) \\ & + k_2 \sum_{x=0}^k \frac{k!}{x!(k-x)!} \lambda_x \lambda_{k-x} + k_2 K_2 W \left[2 \frac{(\lambda_{k+1} - 2^{k+1} S_2 - S_1)}{k+1} \right. \\ & + \frac{(\lambda_k - 2^k S_2 - S_1)}{2} + \sum_{t=1}^{\frac{k-1}{2}} \frac{k}{2} \frac{1}{t} \binom{k}{2t-1} B_t (\lambda_{k-2t+1} - 2^{k-2t+1} S_2 - S_1) \\ & \left. - 2(\lambda_k - 2^k S_2 - S_1) \right] - 2(C - S_1 - S_2) - (\lambda_{k+1} - \lambda_k) - 2k_2 C (\lambda_k - S_1) \\ & + k_3 M \left[\sum_{j=0}^k \frac{k!}{j!(k-j)!} \lambda_{k-j} - (\lambda_k - S_1) \right] \end{aligned}$$

$$\begin{aligned}
& +k_3 \sum_{j=0}^k \frac{(-1)^j k!}{j!(k-j)!} \lambda_{k-j} - \sum_{j=0}^k \frac{(-1)^j k!}{j!(k-j)!} S_1 \\
& - \sum_{j=0}^k \frac{(-1)^j k!}{j!(k-j)!} 2^{k-j} S_2 - (\lambda_k - S_1) \quad (3.9)
\end{aligned}$$

As should be expected, from the 2nd moment onwards, i.e. λ_2 onwards, the calculation of each moment requires a value of the next higher moment.

The above system of equations, either in the moment form or direct form (i.e. $\frac{dS_n}{dt}$) can be used to predict the performance of a plug flow reactor. This part is discussed at length in the next chapter.

Equations for a Continuous Stirred Tank Reactor:

As discussed earlier, the CSTR is relevant to model the top part of the reactor. Both caprolactam and water are fed to the reactor at room temperature and this mixture then boils due to the high temperature at some point in the reactor. The reactor upto this stage then is assumed to behave as a continuous stirred tank reactor. Part of the water fed, evaporates out of the reactor, while any caprolactam that evaporates, is recycled back to the reactor, so that the influence of the evaporation of caprolactam on the kinetics can be neglected. Clearly this is an idealization of the complicated two phase reactor.

Jacobs and Schweigman [10] have given an empirical correlation between the per cent by weight of water in the

reaction mixture, W , at the top of the melt, and the temperature of the reactor in this zone. This correlation is

$$W = 1.76 - 0.0060 T_0 \quad (3.10)$$

where T_0 is the temperature of the melt in this zone. Since perfect mixing is being assumed, W then is also the water content in the exit stream of the CSTR.

When the evaporated caprolactam is recycled, the polymerization process in the CSTR in which the temperature is known, can be described by the following equations:

$$F_i - F_v - F = 0 \quad (1)$$

$$F_i M_i - F M + \rho V r_M = 0 \quad (2)$$

$$F_i C_i - F C + \rho V r_C = 0 \quad (3) \quad (3.11)$$

$$F_i S_{ni} - F S_n + \rho V r_{S_n} = 0 \quad (4)$$

The subscript 'i' in the above equations refers to the inlet conditions. F_v is the flow of water vapour leaving the reactor, and F is the output flow rate of the reaction mass. The 'r's refer to the rate equations for the respective species and are given by the right hand sides of equations (3.2) and (3.3). For a CSTR, since $\frac{\rho V}{F} = \tau$, the residence time, dividing the equations (3.11.2) to (3.11.4) by ρV , we get

$$\frac{M_i}{\tau} - \frac{M}{\tau} + r_M = 0 \quad (1)$$

$$\frac{C_i}{\tau} - \frac{C}{\tau} + r_C = 0 \quad (2) \quad (3.12)$$

$$\frac{S_{ni}}{\tau} - \frac{S_n}{\tau} + r S_n = 0 \quad (3)$$

Since the inlet concentration of polymer chain units is zero the last equation, i.e. (3.12.3) becomes

$$\begin{aligned} \frac{S_n}{\tau} &= r S_n \\ &= k_2 \sum_{m=1}^{n-1} S_{n-m} S_m + 2k_2 K_2 W \sum_{m=n+1}^{\infty} S_m - 2k_2 S_n \sum_{m=1}^{\infty} S_m \\ &\quad - k_2 K_2 W S_n (n-1) + k_3 M (S_{n-1} - S_n) + k_3 K_3 (S_{n+1} - S_n) \end{aligned} \quad n \geq 2 \quad (3.13)$$

Multiplying both sides of the above equation by n^k and summarise from $n=1$ to ∞ yields λ_k/τ on the left-hand side and the right hand side will be the same as the right hand side of eqn.(3.9). From this, the individual moment equations may be obtained by substituting the corresponding values for 'k'. For example:

$$\frac{\lambda_0}{\tau} = k_1 (MW - K_1 S_1) - k_2 (\lambda_0^2 - K_2 W (\lambda_1 - \lambda_0)) \quad (1)$$

$$\frac{\lambda_1}{\tau} = k_1 (MW - K_1 S_1) + k_3 (M \lambda_0 - K_3 (\lambda_0 - S_1)) \quad (2) \quad (3.14)$$

and similar expressions may be written for other moments also.

Substituting the expression for r_M the corresponding rate equation, eqn.(3.12.1) becomes:

$$\frac{M}{\tau} = \frac{M_1}{\tau} - k_1(MW - K_1 S_1) - k_3(M\lambda_0 - K_3(\lambda_0 - S_1)) \quad (3.15)$$

The system of non-linear algebraic equations (3.14) and (3.15) have to be solved by a suitable technique to yield the molecular weight distribution for the case of CSTR. It is to be noted that S_1 still has to be obtained and calculation of λ_k still requires λ_{k+1} .

CSTR Followed by a Plug Flow Reactor:

This is nothing but a combination of the mathematical models written individually for the two cases in the preceding pages. For this combination, the equations for the CSTR are solved first. Values of the concentrations of caprolactam, acid end groups and also the moments are then taken as the initial values for the plug-flow reactor. The corresponding equations for the plug flow reactor are then solved using these initial values and a complete picture of the distribution and concentrations of the various species are obtained.

J. I. KANPUR

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CHAPTER 4

METHOD OF SOLUTION OF THE MODELLING EQUATIONS

In the previous chapter, the formulation of modelling equations, in terms of moments, for the polymerization process, in a CSTR followed by a plug flow reactor was done. It was pointed out that the solution of these equations needed a method for the evaluation of the advanced moments and the concentration of the amino caproic acid, S_1 .

It is possible to integrate the rate equations for S_n (3.3(c)), the concentrations of the chain lengths, directly. Here again, evaluation of S_n requires the evaluation of S_{n+1} . One way of doing this would be to assume the concentration of S_{n+1} to be zero till the concentration of S_n reaches a definite value. For example initially N is taken as 10. S_{11} is assumed to be zero. When S_{10} reaches a small value, say, 0.0001, n is extended to 20 and S_{21} is assumed to be zero and this process is repeated. The difficulty with this method of solution is that it takes a lot of computational time to solve the system of equations especially at high conversions. Also the truncation error or round-off error becomes higher, the larger being the chain length. Hence, recourse has been taken to the method, employing moment equations.

Let us consider a molecular weight distribution function $\mu(v)$, which would generate the k th moment \bar{M}_v^k of continuous chain length variable v :

$$\bar{M}_v^k = \int_0^{\infty} (v)^k \mu(v) dv \quad (4.1)$$

A set of infinite number of moments with an expansion in terms of orthogonal polynomials yields a differential distribution. Min [11] pointed out that the Laguerre polynomials have more general orthogonal properties than the Hermite polynomials because of the possible fractional order of distribution variable within the integrand. The relevant orthogonal properties are:

$$\int_0^{\infty} x \exp(-x) L_n^{\alpha}(x) L_m^{\alpha}(x) dx = \frac{\Gamma(\alpha+n+1)}{n!} \delta_{nm} \quad (4.2)$$

where $L_n^{\alpha}(x)$ is the generalized Laguerre polynomial,

$$L_n^{\alpha}(x) = \sum_{j=0}^n (-1)^j \binom{n+\alpha}{n-j} \frac{(x)^j}{j!} \quad (4.3)$$

and

$$\begin{aligned} \delta_{nm} &= 1 && \text{for } n=m \\ &= 0 && \text{for } n \neq m \end{aligned} \quad (4.4)$$

Any normalized distribution function $G(x)$ can be represented by a choice of Laguerre expansion, as follows:

$$G(x) = \frac{x^{\alpha} \exp(-x)}{\Gamma(\alpha+1)} \sum_{n=0}^{\infty} C_n^{\alpha} L_n^{\alpha}(x) \quad (4.5)$$

But, for smooth distributions, the number of polynomials required is not infinite. Thus the above summation is truncated at some N_{\max} . Now, using the orthogonal properties of Laguerre polynomials, the coefficients C_n^α are correlated to the moments \bar{G}_x^j of the normalized distribution function $G(x)$ by the following expression:

$$C_n^\alpha = \sum_{j=0}^n \frac{(-1)^j \binom{n}{j} \alpha!}{\Gamma(\alpha+j+1)} \bar{G}_x^j \quad (4.6)$$

Min [11] suggested that the free parameter α be so chosen that both C_1^α and C_2^α become zero, resulting in a fast convergence. The expression for α , according to Min [11] is

$$\alpha = -1 + \frac{(\bar{G}_1)^2}{\bar{G}_2 - (\bar{G}_1)^2} \quad (4.7)$$

The normalized distribution function $G(x)$ is related to the original distribution function $M(v)$ by the following expression:

$$M(v) dv = \bar{M}_v^0 G(x) dx \quad (4.8)$$

where \bar{M}_v^0 represents the zeroth moment.

$$v = \frac{(\alpha+1) \bar{M}_v^1}{\bar{M}_v^0} \quad (4.9)$$

The moments of the two distributions, \bar{M}_v and \bar{G}_x are correlated to each other by the expression:

$$\bar{M}_v^k = \bar{M}_v^0 \left[\frac{\bar{M}_v^1}{(\alpha+1)\bar{M}_v^0} \right]^k \bar{G}_x^k \quad (4.10)$$

From the above equations it can be seen that the differential distribution can be approximated from a finite number (N_{\max} to be precise) of integer moments of that distribution by using (4.5) to (4.10). The number of such moments depends upon the complexity of the shape of the distribution. In the present work, N_{\max} was arbitrarily chosen to be 5. Thus reactor modelling will only require λ_6 and S_1 before solution of equations can be obtained. Moments of higher order i.e. 6th and higher ones, can be obtained with the help of eqns. (4.1) to (4.10), by the following equation:

$$\begin{aligned} \bar{G}_x^k &= \int_0^{\infty} x^k G(x) dx \\ &= \frac{\Gamma(\alpha+k+1)}{\Gamma(\alpha+1)} + \frac{1}{\Gamma(\alpha+1)} \sum_{n=3}^{N_{\max}} C_n^{\alpha} \sum_{j=0}^n \\ &\quad (-1)^j \frac{\Gamma(n+\alpha+1) \Gamma(n+k+j+1)}{\Gamma(n-j+1) \Gamma(\alpha+j+1) \Gamma(j+1)} \end{aligned} \quad (4.11)$$

To be specific \bar{G}_x^6 can be obtained if the first five moments are known and then λ_6 of the original molecular weight distribution can be calculated from eqn.(4.10), i.e.

$$\lambda_6 = \lambda_0 \left[\frac{\lambda_1}{\lambda_0(\alpha+1)} \right]^6 \bar{G}_x^6 \quad (4.12)$$

Further, S_1 the concentration of the amino caproic acid, can be evaluated from eqn.(4.8) as

$$S_1 = M(v) \Big|_{v=1} \quad (4.13)$$

Thus λ_6 and λ_6 can be expressed in terms of the other moments, i.e. λ_0 to λ_5 and can be substituted in the system of modelling equations for the batch process. Then modelling simply constitutes the solution of simultaneous differential equations and non-linear algebraic equations.

Once the moments are calculated, the number average and weight average molecular weight, and hence the polydispersity index for the polymer product can be calculated. The expressions for these quantities are as given below:

$$\bar{M}_n = \frac{\lambda_1}{\lambda_0} \quad (4.13)$$

$$\bar{M}_w = \frac{\lambda_2}{\lambda_1} \quad (4.14)$$

$$PDI = \frac{\bar{M}_w}{\bar{M}_n} \quad (4.15)$$

Solution of Modelling Equations for the CSTR-Plug Flow Reactor Combination:

The system of modelling equations for this combination consists of the non-linear algebraic equations (3.13) and (3.15) for the CSTR, and the equations (3.3) and (3.9) for the plug flow reactor.

The per cent by weight of water in the melt at the exit of the CSTR is given by the expression [10]

$$W = 1.76 - 0.0060 T_0 \quad (3.16)$$

So once T_0 is known, the water content can be evaluated.

Conversion of the water content into molar units can be achieved from material balance for water and the total mass balance (See Appendix I).

S_1 and Λ_6 can be determined in terms of the first five moments, as has been just indicated. Now, eqns. (3.13) and (3.15) are a closed set of non-linear algebraic equations which can be solved by following any suitable technique. In the present work, the method suggested by Brown [12] has been made use of for solving the above mentioned equations. The block diagram for Brown's technique is given on the next page.

The residence time in the CSTR was varied from 1 hour to 5 hours. The concentrations of caprolactam, amino caproic acid, acid end groups and the moments were computed for each value of residence time. The output stream of the CSTR is the feed for the plug flow region. From this point onwards, till the end of the reactor, the evaluation of the above mentioned quantities (i.e. the concentrations of the various species and the moments) was done by integrating eqns. (3.3) and (3.10) by Runge Kutta method. \bar{M}_n , \bar{M}_w and PDI were also calculated using the moments.

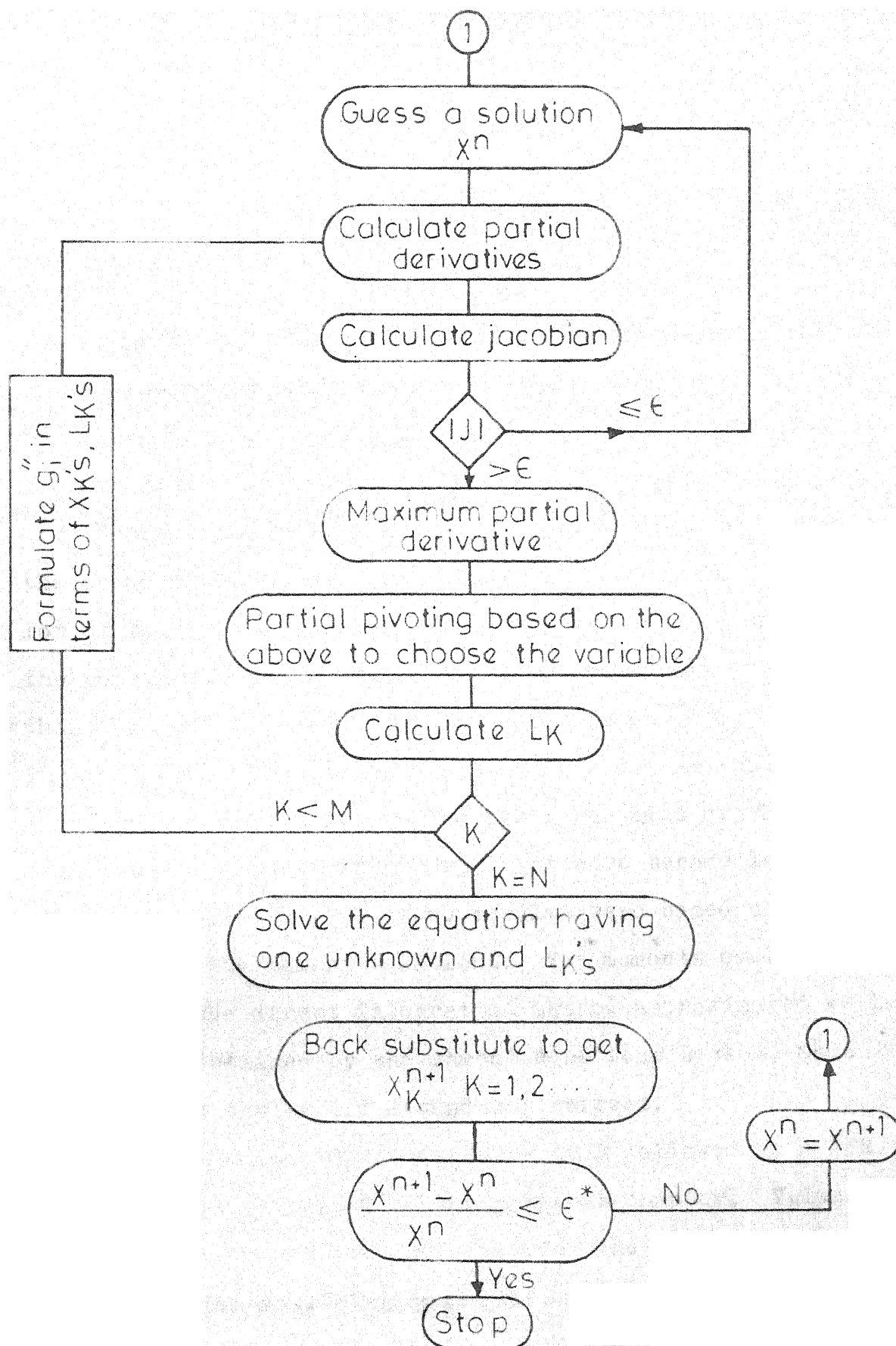


Fig. 1 - Scheme for the solution of CSTR model equation. (Brown's technique)

CHAPTER 5

RESULTS AND DISCUSSION

Direct integration of the rate equations for S_n (the concentration of chain length polymer having n units) was initially tried. In this method it was found that after a certain stage (about 5 hours of reaction time), the number of differential equations which had to be integrated were of the order of 600. (=n referred to on p.22). This consumed lot of time and also caused errors. For example the sum of the concentrations of the individual chain units was less than the acid end group concentration (i.e. $\sum S_n < C$). This difference became larger with increase in reaction time. It is possible that due to the low magnitudes of the concentrations, the round-off errors might have become large. Hence in the present study, all the results were based on the solution of the moment equations. The moments evaluated upto 3 hours by the direct integration method approximated well with those obtained by the moment equations method, thus proving that the second method was correct.

Calculations were made for a CSTR followed by a PFR by the method described in the previous chapter. Values of 1,2,5,4 and 5 hours were selected for the residence time in the CSTR. The following quantities were calculated. Concentrations of the caprolactam and acid end groups, the first

and the second moments. From the moments, the number and weight average molecular weights and hence the polydispersity index were also evaluated. The listing of the computer programs for both the cases have been given in Appendix II (Page No.53). In all the calculations, it has been assumed that feed contains 0.59 moles of water for every 8.75 moles of caprolactam. These figures have been taken from the experimental batch data published by Hermans et al. [1]. This facilitates comparison of the model with the data of Hermans et al. [1].

From the results thus obtained, the per cent conversion of lactam is plotted against the total residence time in the reactor, in Fig.2. Curve I depicts this relationship for a PFR (batch reactor).

The data obtained by Hermans et al. [1] are also shown. It can be seen that the results predicted by the model agree quite well with those obtained by Hermans et al. [1]. Curves II to VI represent the same relationship for a CSTR followed by a PFR, the variable being the residence time in the CSTR. For this system the effective concentration of water in the CSTR (after a certain fraction of the water fed has evaporated) has been determined by the method described in the previous chapter and is found to be 0.236 moles per kg. of the feed mixture to the system. It appears from Fig.2 that the per cent conversion of caprolactam is maximum in the case of the batch reactor. This is so because the water content in the

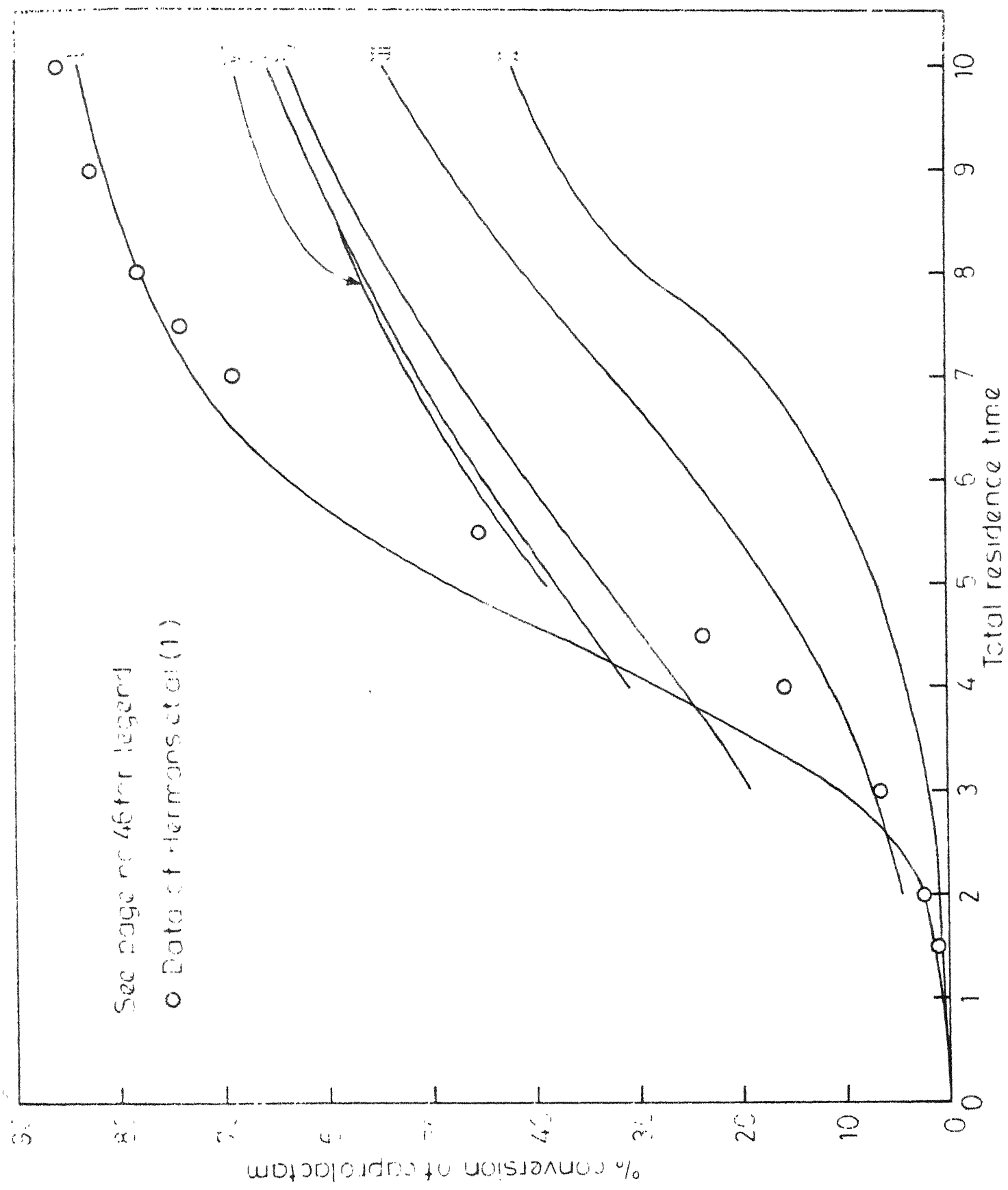


Fig 2 - Effect of total residence time on % conversion of caprolactam.

CSTR-PFR combination system is only 0.236 moles as compared to 0.59 moles in the PFR. Since the concentration of water in the CSTR is low, the ring opening reaction (i.e. the hydrolysis of caprolactam) is reduced to a low level, vindicating the nature of the curves in Fig.2. The per cent conversion in the case of curves II to VI exhibits an increasing trend with an increase in the residence time in the CSTR. Due to the strong mixing effect in the CSTR, the conversion of caprolactam is higher, the longer the reaction mass resides in the CSTR, thus explaining the nature of the curves II to VI in Fig.2.

In Fig.3 the relationship between the total residence time and the number-average molecular weight ^{of} polymer is shown. From the curves it can be seen that the number average molecular weight (\bar{M}_n) of the polymer, in the case of the batch reactor (curve I) is greater than that obtained in the combined system of reactors, in the CSTR of which the residence time is upto 2 hours (curves II and III). But the same curves for the residence times of 3 hours or more (curves IV to VI) show an improvement in the value of \bar{M}_n over the batch system. Since \bar{M}_n is directly proportional to the \bar{DP} of the polymer product, an idea of the \bar{DP} of the product can be obtained from Fig.3. Comparing the curves in Fig.3, it is obvious that for obtaining the same \bar{DP} , there is a reduction in the total residence time

See page no 45 for legend

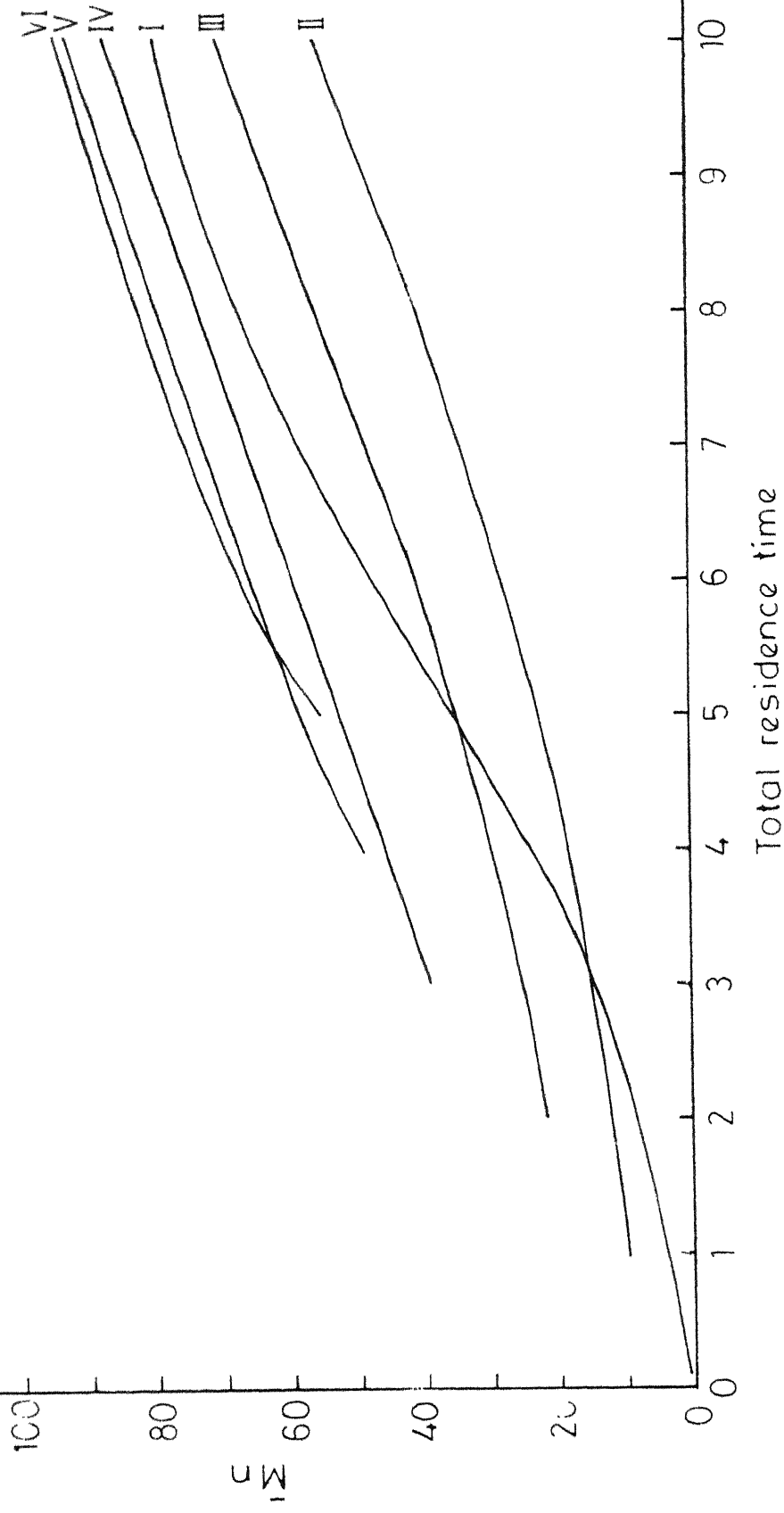


Fig 3 -Effect of total residence time on number average molecular weight

for the CSTR-PFR system with a residence time of 3 hours or more from that of the PFR (batch system). This can be explained by the fact that in the former case, because of the lesser amount of water present in the system, the reverse condensation reaction is checked to a great extent while in the latter (batch system) this is not so. The reason for an increase in \bar{M}_n with an increase in the residence time in the CSTR is as follows: As the residence time increases, concentration of the acid end groups also increases, due to which larger chain-lengths can be obtained through the condensation reaction. If this were not so, part of the PFR is utilised for carrying out the poly addition reaction which does not increase \bar{M}_n rapidly.

A similar kind of behaviour is exhibited in the relationship between the overall reaction time and the weight average molecular weight \bar{M}_w , as shown in Fig.4. Since weight average molecular weight is closely related to the melt viscosity an idea of the melt viscosity can be had from these curves. Jacobs and Schweigman [10] determined the effect of removal of water at various stages of a continuous polymerization process on the relative viscosity of the polymer solution. They also determined the effect on viscosity when the per cent removal of water from the system was varied. They conclude that the increase in the relative viscosity of the polymer solution was higher, the later being the removal of water from

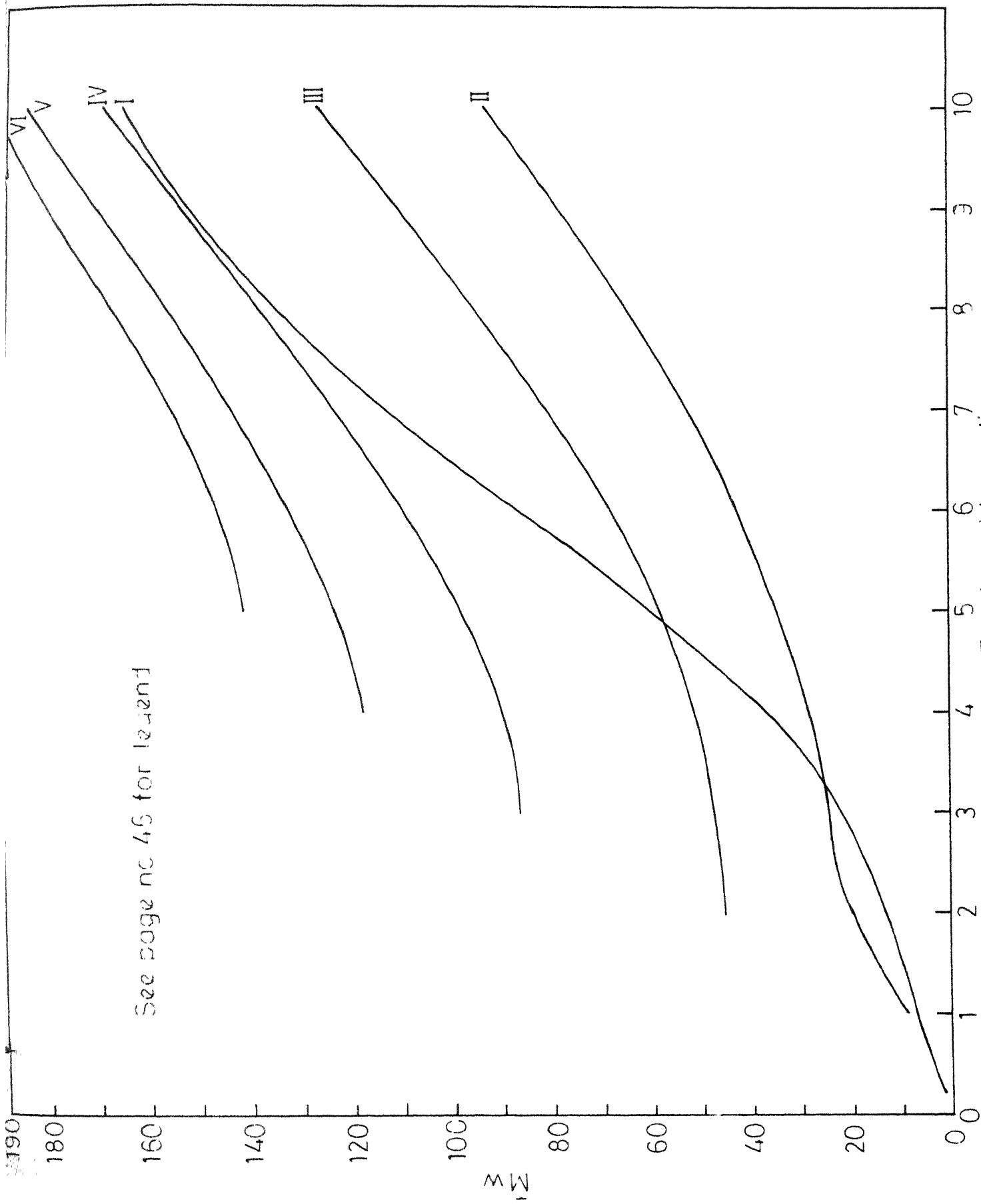


Fig 4 -Effect of total residence time on weight average molecular weight

the system or the greater being the per cent removal of water. In our system the melt viscosity of the polymer has been determined from \bar{M}_w instead of \bar{M}_n , by adopting the method of Kohan [13]. The melt viscosity was then plotted against the total residence time for the CSTR-PFR system for a residence time of 4 hours in the CSTR, as shown in Fig.5. It can be seen that the melt viscosity increases with the total residence time. This data should be of value in modelling the heat transfer and fluid mechanical aspects of the reactor.

A plot connecting the total residence time and the polydispersity index (PDI) is drawn in Fig.6. For the batch reactor the PDI gradually increases to a value of 2.0 at the end of the total residence time. The value of 2 is typical of poly condensation reactions. Kilksen [14] showed that in a stirred tank reactor where irreversible random condensation polymerization occurs, the PDI assumes very high values in the absence of chain terminators, while in the case of the irreversible addition polymerization reaction in a plug flow reactor, the PDI reaches a finite maximum value and then decreases gradually to a constant value. The mechanism of caprolactam polymerization indicates that both condensation and addition polymerization reactions occur simultaneously and moreover, the reactions are reversible. Also, the reactor is modelled to contain the CSTR and the plug flow reactor. Thus the PDI can be expected to attain a reasonably high level in the CSTR

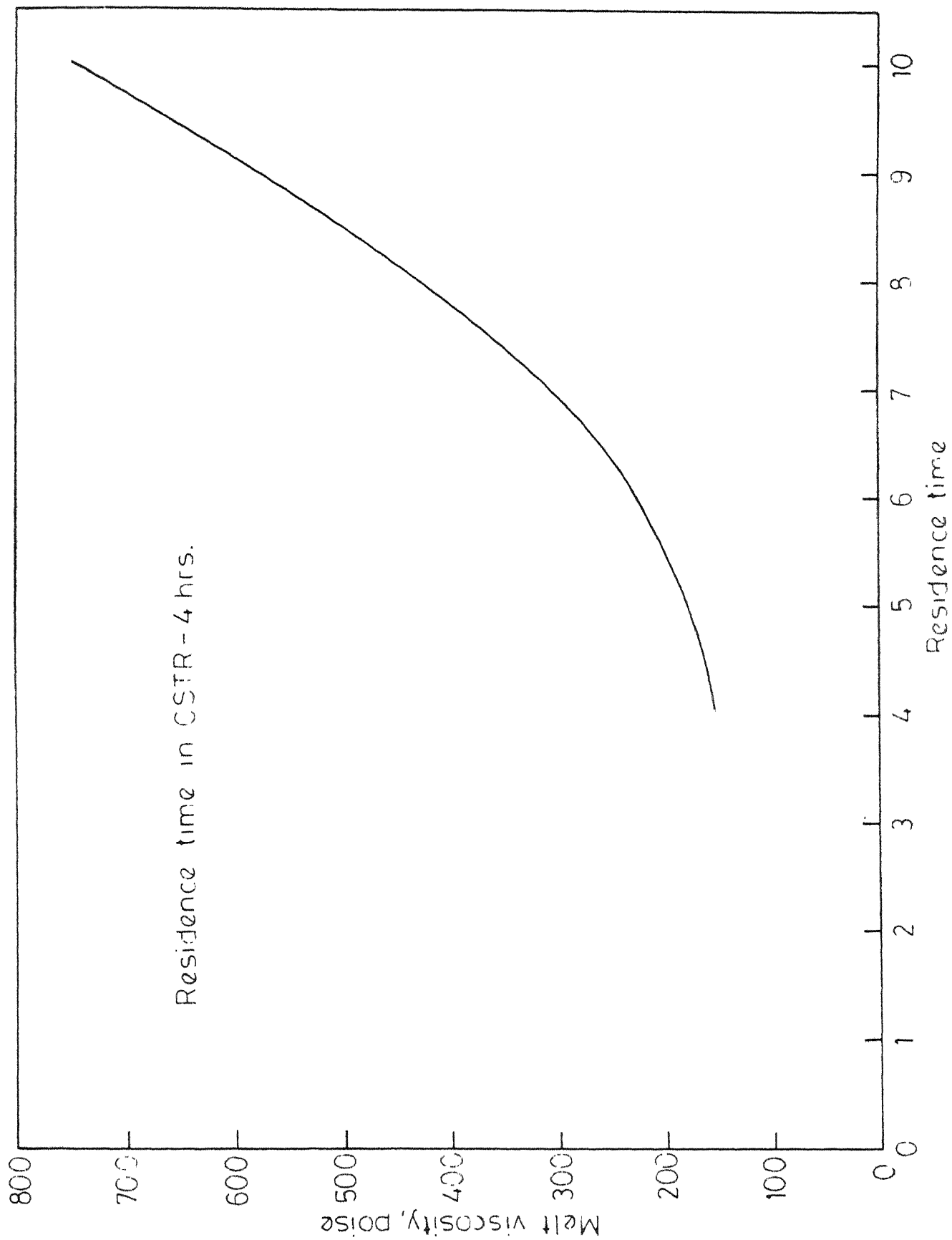


Fig 5 -Effect of total residence time on the polymer melt viscosity.

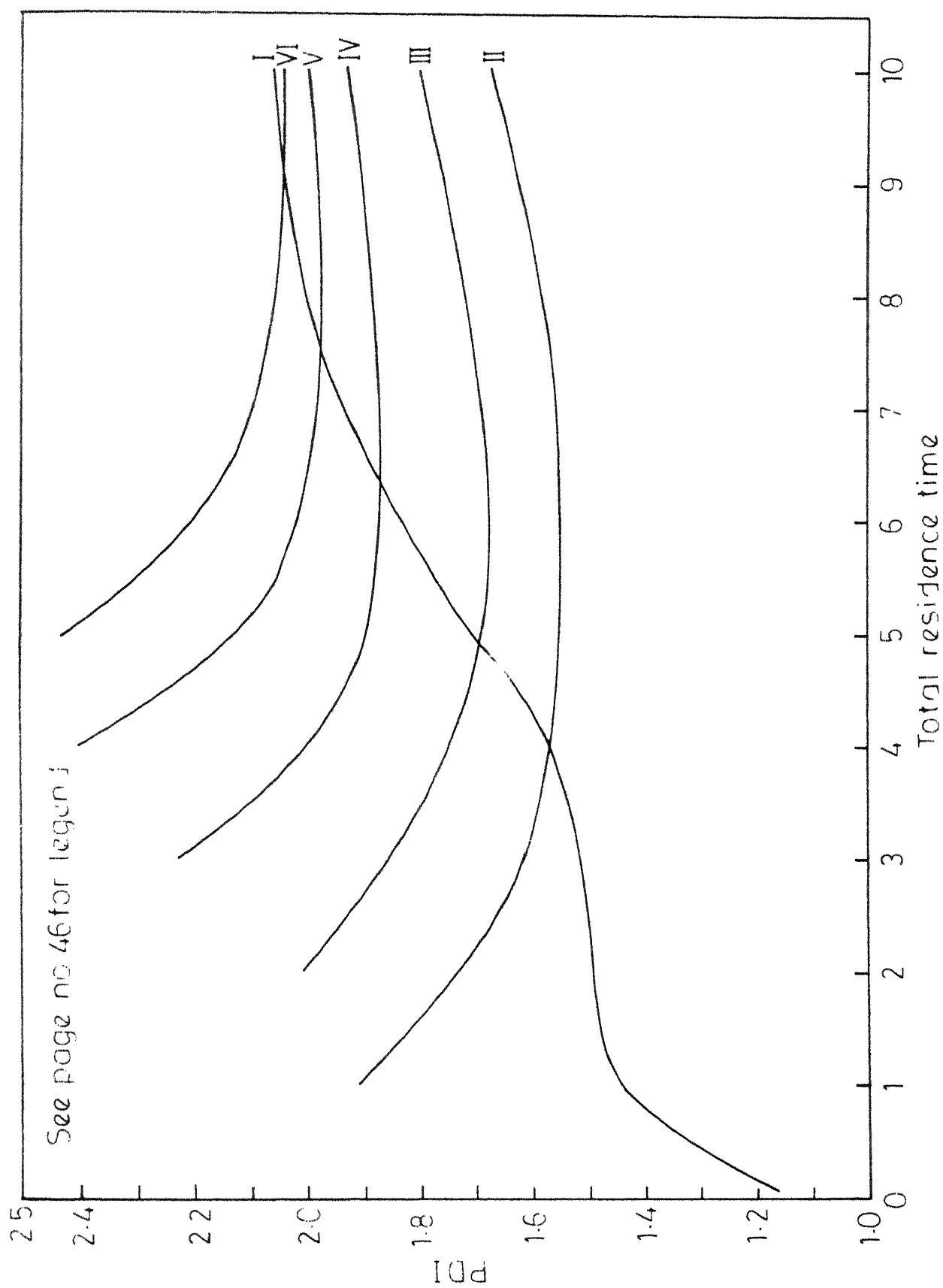


Fig. 6 - Effect of total residence time on polydispersity index.

stage, and once the reaction mixture enters the plug flow region, the distribution can be expected to get narrowed down to a lower level, due to the dominance of the reversible reactions.

The effect of increasing the residence time in the CSTR on various quantities like the per cent conversion of lactam, \bar{M}_n , \bar{M}_w and PDI of the polymer is shown in Fig.7. It can be seen that with increase in the residence time in the CSTR, all the quantities increase. Out of the five values of the residence time chosen in the CSTR stage, the residence time of 4 hours seems to indicate the proper length of time during which the reaction mass can be allowed to react in the CSTR. This conclusion is based on the following: The per cent conversion for this case is nearly the same as that for 5 hours residence time in the CSTR (Fig.2), \bar{M}_n for these two cases is also the same (Fig.3) and PDI reaches a value of 2.0 at the end of the total residence time (Fig.6).

The relationship between the per cent conversion of lactam and (i) the number-average molecular weight, (ii) the weight-average molecular weight and (iii) the polydispersity index, for the reactor models considered have been shown in Figs.8-10. The behaviour of these curves is much similar to that of the curves connecting these quantities and the total residence time, and the discussions made for the latter curves hold good for the former ones also.

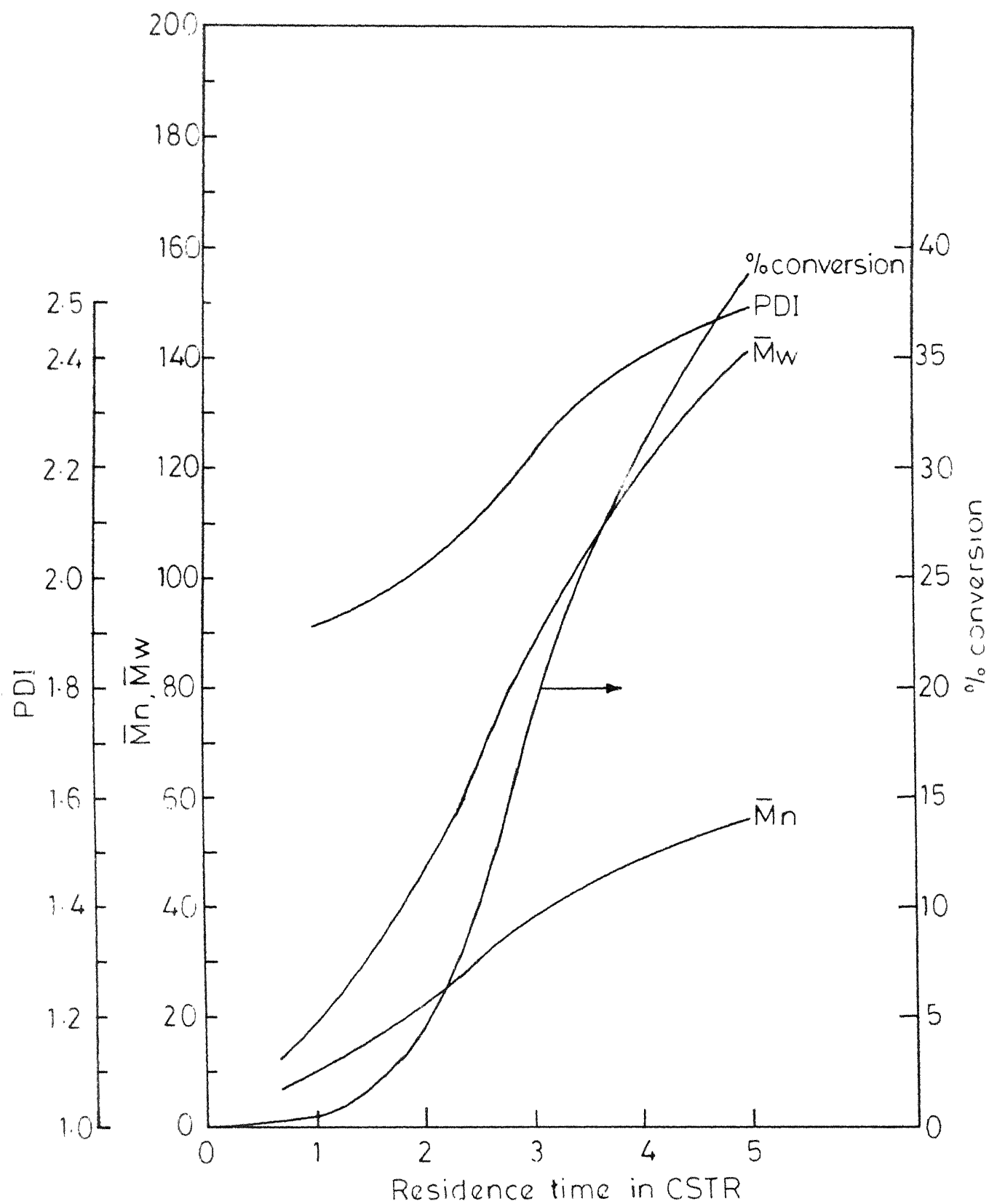


Fig 7 - Effect of residence time in the CSTR on polymer properties

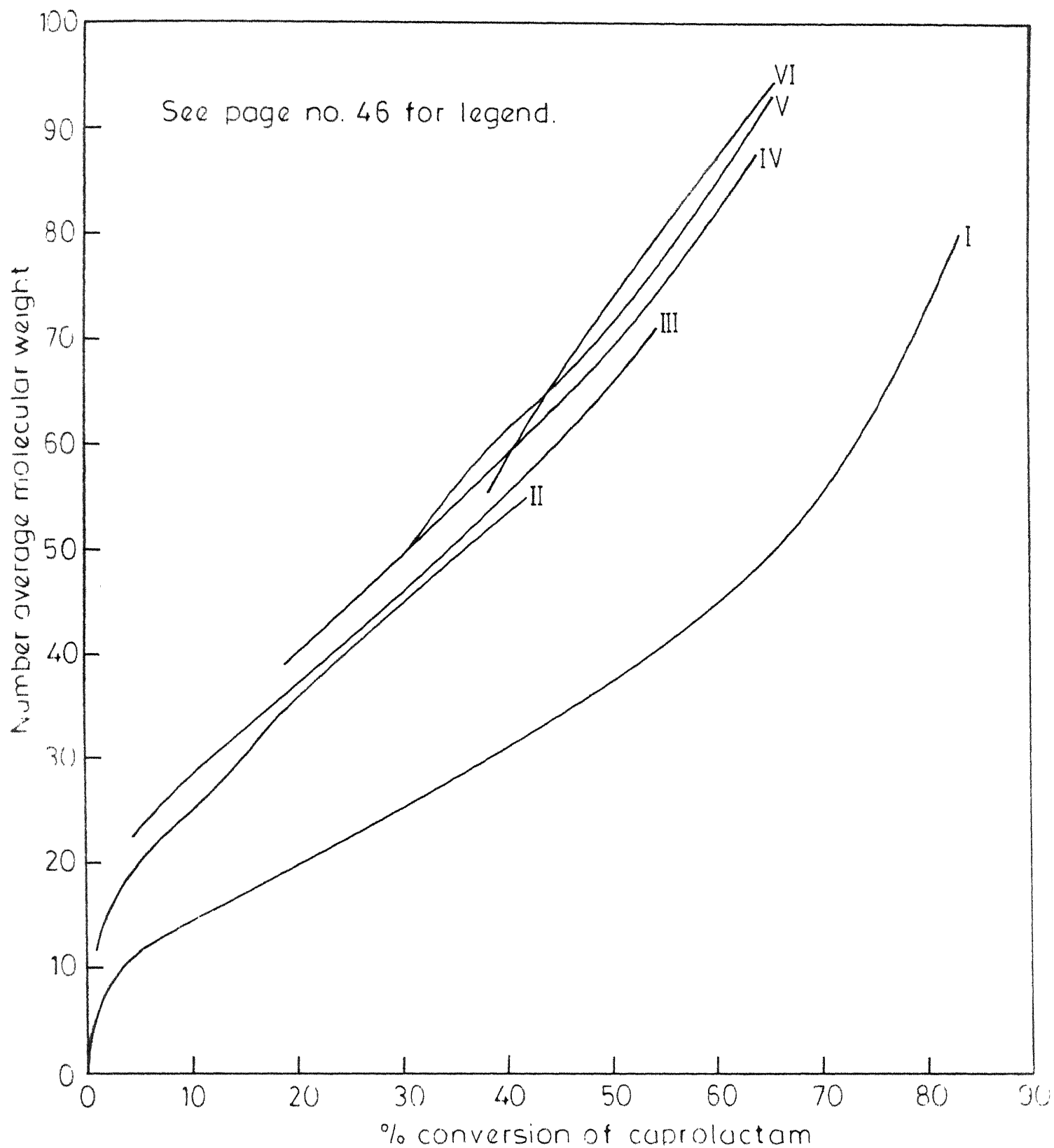


Fig. 8 - Effect of % conversion of caprolactam on number average molecular weight

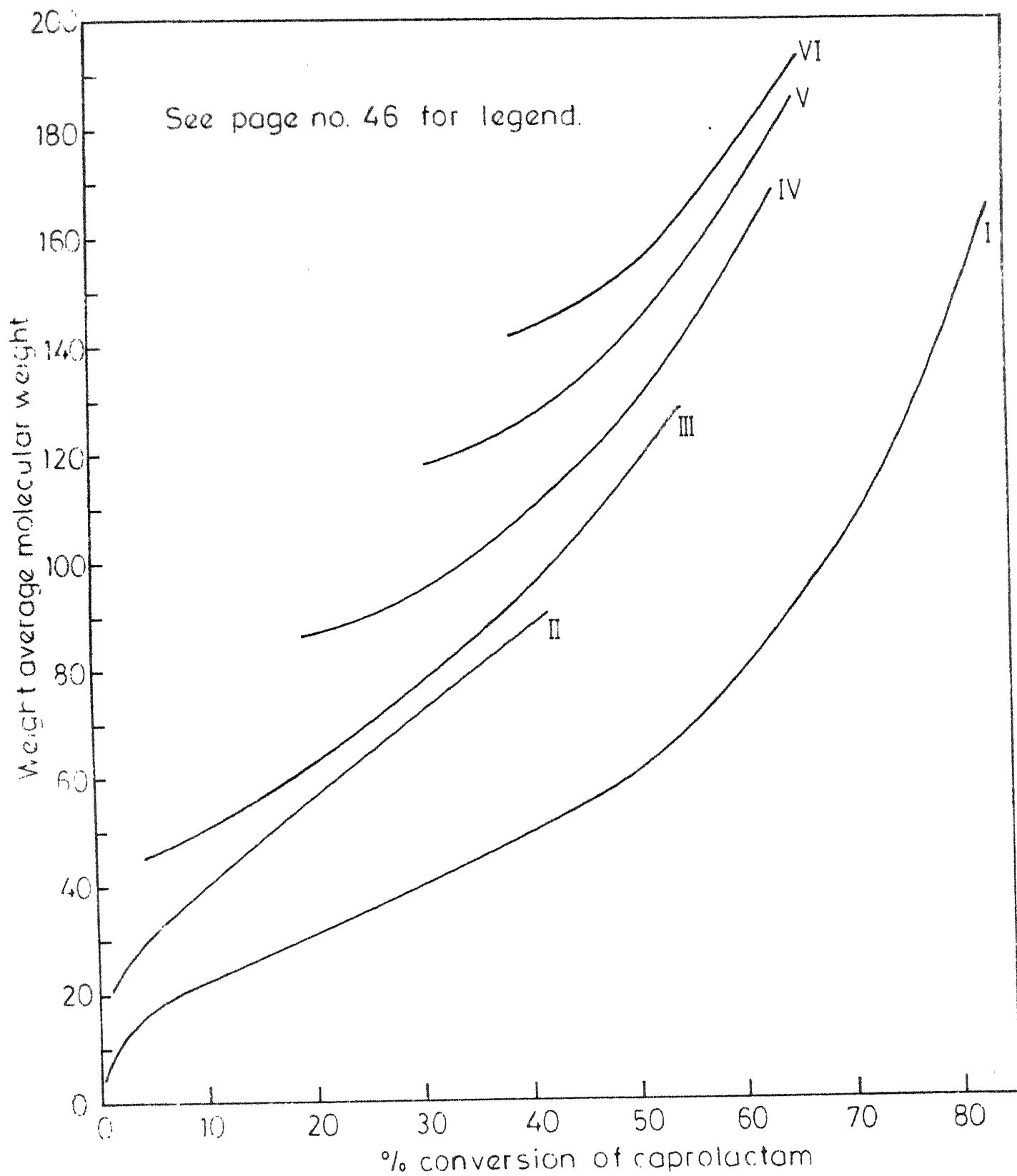


Fig. 9 - Effect of % conversion of caprolactam on weight average molecular weight.

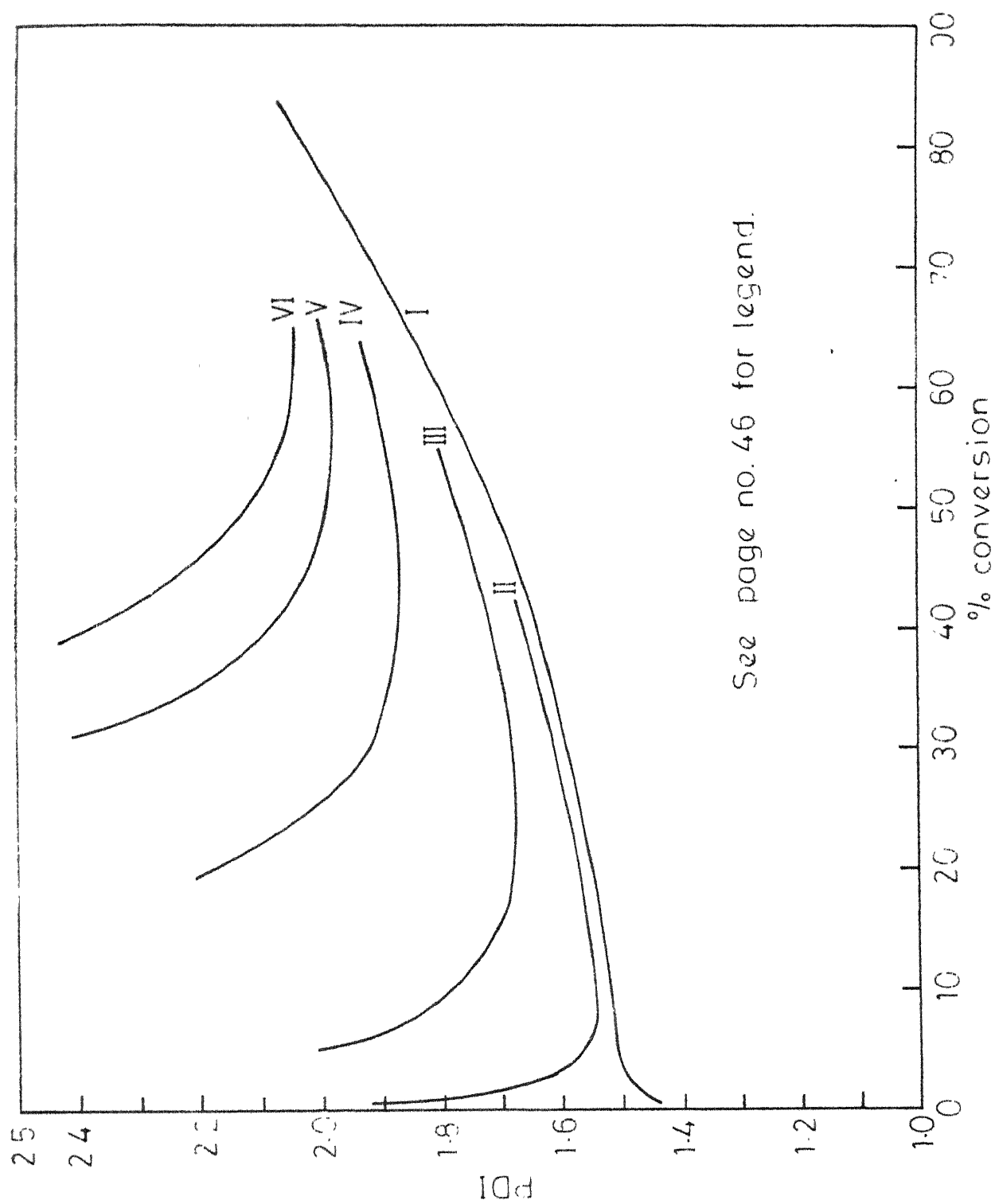


Fig. 10 -Effect of % conversion of caprolactam on polydispersity index

In Fig.10, in which the per cent conversion of caprolactam is plotted against the PDI of the polymer, it can be seen that curves II to VI not only approach the value of 2.0 as the per cent conversion increases, but also approach the behaviour of the batch reactor (curve I), for which the water concentration is higher. This kind of a behaviour seems to indicate that irrespective of the initial water concentration, the PDI of the polymer reaches the same value (about 2.0).

The assumption of Flory's distribution for correlating the concentration of the linear dimer and linear monomer, made by Hoftyzer et al. [5] and Gerdes et al. [7] was investigated from the results obtained. Results are displayed in Table II. It is found that during the initial part of the process, the assumption is incorrect, while towards the end when condensation reaction becomes predominant, the assumption is valid. The other assumption i.e. the concentrations of the linear dimer and linear monomer are equal, made by many workers over the years, has also been found incorrect during the initial stages.

TABLE 2: COMPARISON BETWEEN THE VALUES OF LINEAR MONOMER S_1 AND LINEAR DIMER S_2 (CALCULATED FROM FLORY'S DISTRIBUTION)

[The following table gives the values of S_1 and S_2 calculated from the batch process data].

Time, hr	Concentration of linear monomer, Moles/kg.mixture $S_1 \times 10^2$	Concentration of linear dimer, moles/kg.mixture $S_2 = \frac{(C-S_1)^2}{Z} \times 10^2$
1	0.09236	0.115
2	0.1551	0.251
3	0.1729	0.381
4	0.1564	0.406
5	0.1563	0.327
6	0.1620	0.240
7	0.1595	0.182
8	0.1517	0.146
9	0.1417	0.124
10	0.1355	0.110

LEGEND FOR THE FIGURES 2 - 10

- Curve I Represents the results of the batch reactor (PFR)
- Curves II to VI Represent the results of the CSTR followed by
 the PFR with the residence time in the CSTR being
 the variable
- The variations in the residence time in the
 CSTR are as follows:
- Curve II 1 hour
- Curve III 2 hours
- Curve IV 3 hours
- Curve V 4 hours
- Curve VI 5 hours

CHAPTER 6

CONCLUSION

Two types of reactor configuration have been considered in our study: the batch reactor and a stirred tank reactor followed by a plug flow reactor. Moment equations for the two systems were solved to yield the molecular weight distributions and the moments. It has been found that the PDI was in the region of around 2.0 for the systems considered.

The per cent conversion of caprolactam has been found to be quite low in the case of the system where the stirred tank and plug flow reactors were combined, compared to the batch reactor. This has been found to be due to the reduction in the effective concentration of water in the polymer melt, resulting from the evaporation of water in the CSTR zone. The model, which appears defective due to this, can be corrected by assuming a closed stirred tank reactor followed by a plug flow reactor, with water being removed in between the two reactors.

With the help of the model formulated, it is possible to evaluate properties of the polymer product that have hitherto not been calculated. An assumption for the correlation between the linear dimer and linear monomer that has been made by various other workers, has been avoided in the present model.

CHAPTER 7

SUGGESTIONS FOR FUTURE WORK

The results predicted by this model could not be verified because of lack of sufficient data in the literature. Only the per cent conversion of caprolactam could be compared with the experimental data of Hermans et al. [1]. The following data should be obtained for this purpose:

1. Effect of total residence time in the reactor on the per cent conversion of caprolactam, weight-average molecular weight, PDI and melt viscosity.
2. Effect of varying the residence time in the CSTR on the above mentioned quantities.
3. Various sets of data have been cited in the literature for the reaction rate constants and the corresponding equilibrium constants. Optimization of these constants may be done, since the correct solution of the moments depends to a great extent on choosing the proper values for these constants.
4. Isothermal operation assumed in this work should be relaxed.

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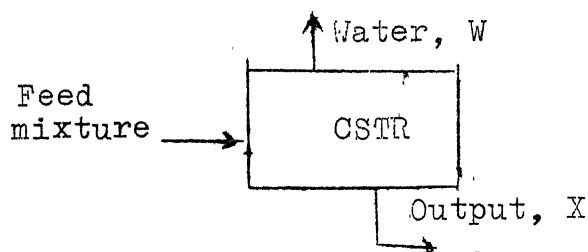
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APPENDIX I

DETERMINATION OF WATER CONTENT IN THE CSTR

Consider the schematic diagram shown below. The feed mixture contains 8.75 moles of caprolactam and 0.59 moles of water.



Hence,

$$\begin{aligned}
 \text{Mass of caprolactam in the feed} &= 8.75 \times \text{Mol. Wt. of caprolactam} \\
 &= 8.75 \times 113 \\
 &= 988.8 \text{ gms}
 \end{aligned}$$

$$\begin{aligned}
 \text{Mass of water in the feed} &= 0.59 \times 18 \\
 &= 10.6 \text{ g}
 \end{aligned}$$

$$\text{Total mass in the feed} = 988.8 + 10.6 = 999.4 \text{ g}$$

Let us assume that W is the mass of water that evaporates out of the reactor and X is the mass of the reaction mixture leaving the CSTR.

Per cent water content in the output mixture is given by [10]

$$W = 1.76 - 0.006 T_0$$

where T_0 is the temperature of the reactor

$$\text{In the present study } T_0 = 221^\circ\text{C}$$

Hence,

$$\begin{aligned} W &= 1.76 - 0.006 \times 221 \\ &= 0.434 \text{ per cent} \end{aligned}$$

Drawing an overall mass balance and a water balance over the CSTR, we get

$$999.4 = W + X$$

$$10.6 = W + \frac{0.434}{100} \times X$$

Solving the two equations, we get

$$X = 993.03 \text{ gms}$$

Hence,

$$\begin{aligned} \text{Water content in the output mixture,} \\ \text{in moles} &= \frac{993.03}{100} \times \frac{0.434}{18} \\ &= 0.236 \end{aligned}$$

APPENDIX II

PROGRAMME LISTING

```

C   SERIES B....W0/XM0=0.067...T=221.5 DEG C
C   MAIN PROGRAM
XM=8.75
XW=0.59
XL0=0.0
XL1=0.0
XL2=0.0
XL3=0.0
XL4=0.0
XL5=0.0
XL6=0.0
DT=1./12.
S1=0.0
T=0.0
    TYPE 90
10   K=0
    TYPE 91,T,XM,XL0,XL1,XL2,XL3,XL4,XL5,XL6,S1,Z,FM1,FM2,PDI
20   T=T+DT
    IF(T.GT.10.0) STOP
    FM11=FM(XL0,XM,S1)*DT
    FL01=FL0(XL0,XL1,XM,S1)*DT
    FL11=FL1(XL0,XM,S1)*DT
    FL21=FL2(XL0,XL1,XL3,XM,S1)*DT
    FL31=FL3(XL0,XL1,XL2,XL4,XM,S1)*DT
    FL41=FL4(XL0,XL1,XL2,XL3,XL5,XM,S1)*DT
    FL51=FL5(XL0,XL1,XL2,XL3,XL4,XL6,XM,S1)*DT
    ZM=XM+FM11
    ZL0=XL0+FL01
    ZL1=XL1+FL11
    ZL2=XL2+FL21
    ZL3=XL3+FL31
    ZL4=XL4+FL41
    ZL5=XL5+FL51
    FM12=FM(ZL0,ZM,S1)*DT
    FL02=FL0(ZL0,ZL1,ZM,S1)*DT
    FL12=FL1(ZL0,ZM,S1)*DT
    FL22=FL2(ZL0,ZL1,ZL3,ZM,S1)*DT
    FL32=FL3(ZL0,ZL1,ZL2,ZL4,ZM,S1)*DT
    FL42=FL4(ZL0,ZL1,ZL2,ZL3,ZL5,ZM,S1)*DT
    FL52=FL5(ZL0,ZL1,ZL2,ZL3,ZL4,XL6,ZM,S1)*DT
    XM=XM+(FM11+FM12)/2.
    XL0=XL0+(FL01+FL02)/2.
    XL1=XL1+(FL11+FL12)/2.
    XL2=XL2+(FL21+FL22)/2.
    XL3=XL3+(FL31+FL32)/2.
    XL4=XL4+(FL41+FL42)/2.
    XL5=XL5+(FL51+FL52)/2.
    XW=0.59-XL0
    Z=XL1-XL0
    FM1=XL1/XL0
    FM2=XL2/XL1
    PDI=FM2/FM1
    ZAZ=-1.+XL1**2/(XL0*XL2-XL1**2)
    CALL DS61(XL0,XL1,XL2,XL3,XL4,XL5,XL6,S1)
    IF(S1.GE.0.) GO TO 123

```

```

123 S1=0.0
CONTINUE
IF(XL0.EQ.0..OR.XL1.EQ.0.) GO TO 50
IF(XL2.EQ.0..OR.XL3.EQ.0.) GO TO 50
IF(XL4.EQ.0..OR.XL5.EQ.0.) GO TO 50
50 CONTINUE
GO TO 10
90 FORMAT(4X,'TIME',5X,'M',7X,'LAMDA0',6X,'LAMDA1',6X,'LAMDA2',
16X,'LAMDA3',4X,'LAMDA4',5X,'LAMDA5',6X,'LAMDA6',8X,'S1',
29X,'Z',6X,'EM1',7X,'EM2',5X,'PDI',1X,140(1H-))
91 FORMAT(2X,F6.4,13(2X,E9.4))
GO TO 20
STOP
END
C FUNCTION A CALCULATES ALPHA
C *****
FUNCTION A(D0,D1,D2)
A=-1.+(D1**2)/(D0*D2-D1**2)
RETURN
END
C *****
C FUNCTION G(XB)
C *****
CALL GAMA(XB,GB,IJ)
G=GB
RETURN
END
C TO CALCULATE C3A,C4A,C5A
C SUBROUTINE CF345(G1,G2,G3,G4,G5,F,C3,C4,C5,G6)
C *****
DIMENSION P(20),E(20)
DO 10 I=1,12
RBY=I
E(I)=G(RBY)
C=F+I
P(1)=G(8)
10 T32=3.*P(1)*G1/P(2)
T33=3.*P(1)*G2/P(3)
T34=P(1)*G3/P(4)
C3=1-T32+T33-T34
C *****
T42=T32*4./3.
T43=T33*2.
T44=T34*4.
T45=P(1)*G4/P(5)
C4=1-T42+T43-T44+T45
C *****
T52=T32*5./3.
T53=T33*10./3.
T54=T34*10.
T55=T45*5.
T56=P(1)*G5/P(6)
C5=1-T52+T53-T54+T55-T56
C *****
T1=P(7)/P(1)

```

```

T2=P(4)*P(7)/(E(4)*P(1)*E(1))
T3=P(4)*P(8)/(E(3)*P(2)*E(2))
T4=P(4)*P(9)/(E(2)*P(3)*E(3))
T5=P(4)*P(10)/(E(1)*P(4)*E(4))
T6=P(5)*P(7)/(E(5)*P(1)*E(1))
T7=P(5)*P(8)/(E(4)*P(2)*E(2))
T8=P(5)*P(9)/(E(3)*P(3)*E(3))
T9=P(5)*P(10)/(E(2)*P(4)*E(4))
T10=P(5)*P(11)/(E(1)*P(5)*E(5))
T11=P(6)*P(7)/(E(6)*P(1)*E(1))
T12=P(6)*P(8)/(E(5)*P(2)*E(2))
T13=P(6)*P(9)/(E(4)*P(3)*E(3))
T14=P(6)*P(10)/(E(3)*P(4)*E(4))
T15=P(6)*P(11)/(E(2)*P(5)*E(5))
T16=P(6)*P(12)/(E(1)*P(6)*E(6))
TT1=C3*(T2-T3+T4-T5)
TT2=C4*(T6-T7+T8-T9+T10)
TT3=C5*(T11-T12+T13-T14+T15-T16)
G6=TT1+(1./P(1))*(TT1+TT2+TT3)
RETURN
END

```

```

*****
THIS SUBROUTINE GIVES THE VALUE OF LAMDA6,S1 WITH LAMDAS 0 TO 5 AS
INPUT
*****

```

```

SUBROUTINE DS61(D0,D1,D2,D3,D4,D5,D6,S)
DIMENSION Y(50)
REAL LX3,LX4,LX5
F=A(D0,D1,D2)
F STANDS FOR ALPHA
GX0=1.0
DEFINE
DD=D0*D2-D1**2
GX1=(D1**2)/DD
GX2=(D1**2)*(D0*D2)/(DD**2)
GX3=(D0**2)*(D1**3)*(D3)/(DD**3)
GX4=(D0**3)*(D1**4)*(D4)/(DD**4)
GX5=(D0**4)*(D1**5)*D5/(DD**5)
CF0=1.0
CALL CF345(GX1,GX2,GX3,GX4,GX5,F,CF3,CF4,CF5,GX6)
D6=GX6*((D0*D2-(D1**2))**6)/((D1**6)*(D0**5))
X=(F+1)*D0/D1
DO 10 I=1,6
Y(I)=F+I
LX3=Y(3)*Y(2)*Y(1)/6.-Y(3)*Y(2)*Y(1)*D0/(2.*D1)+Y(3)*(Y(1)**2)*(D0
1**2)/(2.*(D1**2))-Y(1)**3*(D0**3)/(6.*D1**3)
LX4=Y(4)*Y(3)*Y(2)*Y(1)/24.-Y(4)*Y(3)*Y(2)*Y(1)*D0/(6.*D1)+Y(4)*
1Y(3)*(Y(1)**2)*(D0**2)/(4.*D1**2)-Y(4)*(Y(1)**3)*(D0**3)/(6.*D1**3
2)+Y(1)**4*D0**4/(24.*D1**4)
LX5=Y(5)*Y(4)*Y(3)*Y(2)*Y(1)/120.-Y(5)*Y(4)*Y(3)*Y(2)*Y(1)*D0/(24.
1*D1)+Y(5)*Y(4)*Y(3)*Y(1)**2*D0**2/(12.*D1**2)-Y(5)*Y(4)*Y(1)**3*D0
2**3/(12.*D1**3)+Y(5)*Y(1)**4*D0**4/(24.*D1**4)-Y(1)**5*D0**5/(120.
3*D1**5)
O=F+1
O0=G(O)

```

```
GG=(Q*D0/D1)**F*EXP(-Q*D0/D1)*((1+CF3*LX3+CF4*LX4+CF5*LX5)/Q0
S=D0**2*Q*GG/D1
```

```
RETURN
END
```

```
*****
SCKS TAKES IN C AS INPUT AND GIVES SK1,SK2,SK3,CK1,CK2,CK3,W AS
OUTPUT
```

```
SUBROUTINE SCKS(C,PK1,PK2,PK3,OK1,OK2,OK3,OW)
```

```
PK1=0.00085+0.211*C
```

```
PK2=0.937+17.014*C
```

```
PK3=1.041+22.82*C
```

```
OK1=382.0
```

```
OK2=1./720.
```

```
OK3=0.9
```

```
OW=0.59-C
```

```
RETURN
```

```
END
```

```
*****
```

```
FUNCTION FM(XL0,XM,S1)
```

```
CALL SCKS(XL0,SK1,SK2,SK3,CK1,CK2,CK3,W)
```

```
FM=-SK1*(XM*W-CK1*S1)-SK3*(XM*XL0-CK3*(XL0-S1))
```

```
RETURN
```

```
END
```

```
*****
```

```
FUNCTION FLO(XL0,XL1,XM,S1)
```

```
CALL SCKS(XL0,SK1,SK2,SK3,CK1,CK2,CK3,W)
```

```
FLO=SK1*(XM*W-CK1*S1)-SK2*(XL0**2-CK2*W*(XL1-XL0))
```

```
RETURN
```

```
END
```

```
FUNCTION FL1(XL0,XM,S1)
```

```
CALL SCKS(XL0,SK1,SK2,SK3,CK1,CK2,CK3,W)
```

```
FL1=SK1*(XM*W-CK1*S1)+SK3*(XM*XL0-CK3*(XL0-S1))
```

```
RETURN
```

```
END
```

```
FUNCTION FL2(XL0,XL1,XL3,XM,S1)
```

```
CALL SCKS(XL0,SK1,SK2,SK3,CK1,CK2,CK3,W)
```

```
TZ1=SK1*(XM*W-CK1*S1)+2.*SK2*XL1**2
```

```
TZ2=SK2*CK2*W*(XL1-XL3)/3.+SK3*XM*(XL0+2.*XL1)
```

```
TZ3=SK3*CK3*(XL0+S1-2.*XL1)
```

```
FL2=TZ1+TZ2+TZ3
```

```
RETURN
```

```
END
```

```
FUNCTION FL3(XL0,XL1,XL2,XL4,XM,S1)
```

```
CALL SCKS(XL0,SK1,SK2,SK3,CK1,CK2,CK3,W)
```

```
TZ1=SK1*(XM*W-CK1*S1)+6.*SK2*XL1*XL2+0.5*SK2*CK2*W*(XL2-XL4)
```

```
TZ2=SK3*XM*(3.*XL1+3.*XL2+XL0)
```

```
TZ3=SK3*CK3*(3.*XL1-3.*XL2-XL0+S1)
```

```
FL3=TZ1+TZ2+TZ3
```

```
RETURN
```

```
END
```

```
FUNCTION FL4(XL0,XL1,XL2,XL3,XL5,XM,S1)
```

```
CALL SCKS(XL0,SK1,SK2,SK3,CK1,CK2,CK3,W)
```

```
TZ1=SK1*(XM*W-CK1*S1)+SK2*(8.*XL1*XL3+6.*XL2*XL2)
```

```
TZ2=SK2*CK2*W*(2.*XL3/3.+XL1/15.-3.*XL5/5.)
```

```
TZ3=SK3*XM*(4.*XL1+6.*XL2+4.*XL3+XL0)
```

```

TZ4=SK3*CK3*(-4.*XL1+6.*XL2-4.*XL3+XL0+S1)
FL4=TZ1+TZ2+TZ3+TZ4
RETURN
END
FUNCTION FL5(XL0,XL1,XL2,XL3,XL4,XL6,XM,S1)
CALL SCKS(XL0,SK1,SK2,SK3,CK1,CK2,CK3,W)
TZ1=SK1*(XM*W-CK1*S1)+SK2*(10.*XL1*XL4+20.*XL2*XL3)
TZ2=SK2*CK2*W*(-XL2/6.+5.*XL4/6.-2.*XL6/3.)
TZ3=SK3*XM*(5.*XL1+10.*(XL2+XL3)+5.*XL4+XL0)
TZ4=SK3*CK3*(5.*(XL1-XL4)+10.*(XL3-XL2)-XL0+S1)
FL5=TZ1+TZ2+TZ3+TZ4
RETURN
END

```

```

C *****
C SUBROUTINE GAMA(XX,GX,IER)
C *****
C XX=THE ARGUMENT FOR THE GAMA FUNCTION
C GX=THE RESULTANT GAMA FUNCTION VALUE
C IER=0.....NO ERROR
C IER=1.....LESS THAN E-06 OF BEING A NEGATIVE NUMBER
C IER=2.....XX,GT.57, OVERFLOW GX SET TO 1.0E75
C *****
4 IF(XX-57.) 6,6,4
4 IER=2
GX=0.1E 36
TYPE 91
91 FORMAT(/10X,'ARGUMENT OF SUB.GAMA GT.57'/)
6 RETURN
X=XX
ERR=1.0E-6
GX=1.0
10 IF(X-2.0) 50,50,15
15 IF(X-2.0) 110,110,15
X=X-1.0
GX=GX*X
GO TO 10
50 IF(X-1.0) 60,120,110
60 IF(X-ERR) 62,62,80
62 Y=FLOAT(INT(X))-X
IF(ABS(Y)-ERR) 130,130,64
64 IF(1.0-Y-ERR) 130,130,70
70 IF(X-1.0) 80,80,110
80 GX=GX/X
X=X+1.0
GO TO 70
110 Y=X-1.0
GY=1.0+Y*(-0.5771017+Y*(+0.985854+Y*(-0.8764218+Y*(0.8328212+Y*(-0
1.5684729+Y*(+0.2548205+Y*(-0.0514993))))))
GX=GX*GY
120 RETURN
130 IER=1
RETURN
END

```

```

C ***** MAIN PROGRAM *****
C DIMENSION X(9)
C READ(1,*)(X(L),L=1,7)
C READ(1,*)EPS
C CALL NONLIN(7,4,25,1,X,EPS)
C STOP
C END
C *****
C SUBROUTINE NONLIN(N,NUMSIG,MAXIT,IPRINT,X,EPS)
C THIS SUBROUTINE SOLVES A SYSTEM OF N SIMULTANEOUS NONLINEAR
C EQUATIONS.
C INPUT PARAMETERS FOLLOW.
C N=NUMBER OF EQUATIONS(=NO. OF UNKNOWN).
C NUMSIG=NO. OF SIGNIFICANT DIGITS DESIRED.
C MAXIT=MAXIMUM NUMBER OF ITERATIONS TO BE ALLOWED.
C ITYPE=OUTPUT OPTION, OUTPUT IF=1,FAILURE INDICATIONS ARE
C ALWAYS OUTPUT;MAXIT EXCEEDED AND SINGULAR JACOBIAN.
C X=VECTOR OF INITIAL GUESSES.
C EPS=CONVERGENCE CRITERION. ITERATION WILL BE TERMINATED
C IF ABS(F(I)).LT.EPS, I=1,2,...,N, WHERE F(I) DENOTES THE
C I-TH FUNCTION IN THE SYSTEM.
C
C OUTPUT PARAMETERS FOLLOW.
C MAXIT=NO. OF ITERATIONS USED.
C X=SOLUTION OF THE SYSTEM (OR BEST APPROXIMATION THERETO)
C *****
C DELTA WILL BE A FUNCTION OF THE MACHINE AND THE PRECISION USED.
C REAL X(10),PART(10),TEMP(15),RELCON,F,FACTOR,HOLD,H,FPLUS,DERMAX
C DIMENSION ISUB(30),LOOKUP(30,30),COE(30,31)
C DELTA=1.E-07
C RELCON=10.F+0*(-NUMSIG)
C JFEST=1
C DO700 F=1,MAXIT
C IQUIT=0.
C FMAX=0.
C M1=M-1
C IF(IPRINT.NE.1) GOTO 9
C TYPE49,M1,(X(I),I=1,N)
C9 FORMAT(1X,I5,3E18.8/(E23.8,2E18.8))
C
C9 DO 10 J=1,N
C10 LOOKUP(1,J)=J
C DO500 K=1,N
C IF(K-1) 134,134,131
C131 KMIN=K-1
C CALL BACK(KMIN,N,X,ISUB,COE,LOOKUP)
C SET UP THE PARTIAL DERIVATIVES OF KTH FUNCTION
C134 CALL AUXFCN(X,F,K)
C FMAX=AMAX1(FMAX,ABS(F))
C IF(ABS(F).GE.EPS) GO TO 1345
C IQUIT=IQUIT+1
C IF(IQUIT.NE.N) GO TO 1345
C GO TO 725
C1345 FACTOR=0.001E+00
C135 ITALLY=0

```



```

DO 200 I=K,N
ITEMP=LOOKUP(K,I)
HOLD=X(ITEMP)
PREC=5.E-6
C PREC IS A FUNCTION OF THE MACHINE SIGNIFICANCE.
ETA=FACTOR*ABS(HOLD)
H=AMIN1(FMAX,ETA)
IF(H.LT.PREC) H=PREC
X(ITEMP)=HOLD+H
IF(K-1)161,161,151
151 CALL BACK(KMIN,N,X,ISUB,COE,LOOKUP)
161 CALL AUXFCN(X,FPLUS,K)
PART(ITEMP)=(FPLUS-F)/H
X(ITEMP)=HOLD
IF(ABS(PART(ITEMP)).LT.DELTA) GO TO 190
IF(ABS(F/PART(ITEMP)).LE.1.E+15) GO TO 200
190 ITALLY=ITALLY+1
200 CONTINUE
IF(ITALLY.LE.(N-K)) GOTO 202
FACTOR=FACTOR*10.0E+00
IF(FACTOR.GT.11.) GO TO 775
GO TO 135
202 IF(K.LT.N) GO TO 203
IF(ABS(PART(ITEMP)).LT.DELTA) GO TO 775
COE(K,N+1)=0.0E+00
KMAX=ITEMP
GO TO 500
C FIND PARTIAL DERIVATIVE OF LARGEST ABSOLUTE VALUE.
203 KMAX=LOOKUP(K,K)
DERMAX=ABS(PART(KMAX))
KPLUS=K+1
DO 210 I=KPLUS,N
JSUB=LOOKUP(K,I)
TEST=ABS(PART(JSUB))
IF(TEST.LT.DERMAX) GO TO 209
DERMAX=TEST
LOOKUP(KPLUS,I)=KMAX
KMAX=JSUB
GO TO 210
209 LOOKUP(KPLUS,I)=JSUB
210 CONTINUE
TM=PART(KMAX)
IF(ABS(TM).EQ.0.0) GO TO 775
C SETTING UP OF COEFFICIENTS FOR KTH ROW OF TRIANGULAR LINEAR
ISUB(K)=KMAX
COE(K,N+1)=0.0E+00
DO 220 J=KPLUS,N
JSUB=LOOKUP(KPLUS,J)
COE(K,JSUB)=-PART(JSUB)/PART(KMAX)
COE(K,N+1)=COE(K,N+1)+PART(JSUB)*X(JSUB)
220 CONTINUE
500 COE(K,N+1)=(COE(K,N+1)-F)/PART(KMAX)+X(KMAX)
C BACK SUBSTITUTION TO OBTAIN NEXT APPROXIMATION TO X
C SYSTEM USED TO BACK SOLVE FOR THE FIRST K VALUES OF X(I)

```

```

      IF(N.EQ.1) GO TO 610
      CALL BACK(N-1,N,X,ISUB,COE,LOOKUP)
      IF(M=1) 650,650,625
      C TEST FOR CONVERGENCE.
      625 DO 630 I=1,N
      IF(ABS(TEMP(I)-X(I)).GT.ABS(X(I))*RELCON) GO TO 649
      630 CONTINUE
      JTEST=JTEST+1
      IF(JTEST-3) 650,725,725
      649 JTEST=1
      650 DO 660 I=1,N
      660 TEMP(I)=X(I)
      700 CONTINUE
      TYPE 1753
      1753 FORMAT(1X,'NO CONVERGENCE. MAXIMUM NUMBER OF ITERATIONS USED')
      IF(IPRINT.NE.1) GO TO 800
      TYPE 1763
      1763 FORMAT(1X,'FUNCTION VALUES AT THE LAST APPROXIMATION FOLLOW')
      IFLAG=1
      GO TO 7777
      725 IF(IPRINT.NE.1) GO TO 800
      7777 DO 750 K=1,N
      CALL AUXFCN(X,PART(K),K)
      750 CONTINUE
      IF(IFLAG.NE.1) GOTO 8777
      TYPE 7788,(PART(K),K=1,N)
      7788 FORMAT(3E20.8)
      GO TO 800
      8777 TYPE 751
      751 FORMAT(//'CONVERGENCE HAS BEEN ACHIEVED. THE FUNCTION VALUES')
      TYPE 7515,(PART(K),K=1,N)
      7515 FORMAT(1X,'AT THE FINAL APPROXIMATION FOLLOW'//(3E20.8))
      GO TO 800
      775 TYPE 752
      752 FORMAT('MODIFIED JACOBIAN IS SINGULAR. TRY A DIFFERENT')
      TYPE 7525
      7525 FORMAT('INITIAL APPROXIMATION.')
```

800 MAYIT=M1+1
 CALL AUXFCN(X,Y,109)
 STOP
 END

```

C *****
C SUBROUTINE BACK(KMIN,N,X,ISUB,COE,LOOKUP)
C SUBROUTINE BACK SOLVES THE FIRST KMIN ROWS OF A TRIANGULARISED
C LINEAR SYSTEM FOR IMPROVED X VALUES IN TERMS OF PREVIOUS ONES.
  DIMENSION X(30),COE(30,31)
  DIMENSION ISUB(30),LOOKUP(30,30)
  DO 200 KK=1,KMIN
    KM=KMIN-KK+2
    KMAX=ISUB(KM-1)
    X(KMAX)=0.0E+00
    DO 100 J=KM,N
      JSUB=LOOKUP(KM,J)
      X(KMAX)=X(KMAX)+COE(KM-1,JSUB)*X(JSUB)
  100 CONTINUE
```

```

200 X(KMAX)=X(KMAX)+COE(KM-1,N+1)
      CONTINUE
      RETURN
      END
C *****
      SUBROUTINE AUXFCN(X,Y,K)
      DIMENSION X(9)
      EM=X(1); D0=X(2); D1=X(3); D2=X(4); D3=X(5); D4=X(6); D5=X(7)
      D6=X(8); S1=X(9)
      EMI=8.75; W=0.236; T=2.0
      CALL SCKS(D0,SK1,SK2,SK3,CK1,CK2,CK3)
      CALL DS61(D0,D1,D2,D3,D4,D5,D6,S)
      IF(K.GT.100) GO TO 888
      GO TO (1,2,3,4,5,6,7),K
1     Y=-EM*(1./T+SK1*W+SK3*D0)+EMI/T+S1*(SK1*CK1-SK3*CK3)+SK3*CK3*D0
      GO TO 80
2     Y=-D0/T+SK1*(EM*W-CK1*S1)-SK2*(D0**2.-CK2*W*(D1-D0))
      GO TO 80
3     Y=-D1/T+SK1*(EM*W-CK1*S1)+SK3*(EM*D0-CK3*(D0-S1))
      GO TO 80
4     Y=-D2/T+SK1*(EM*W-CK1*S1)+2.*SK2*D1**2.+SK2*CK2*W*(D1-D3)/3.+SK3*
1EM*(D0+2.*D1)+SK3*CK3*(D0+S1-2.*D1)
      GO TO 80
5     Y=-D3/T+SK1*(EM*W-CK1*S1)+6.*SK2*D1*D2+SK2*CK2*W*(D2-D4)/2.+
1SK3*EM*(3.*(D1+D2)+D0)+SK3*CK3*(3.*(D1-D2)-D0+S1)
      GO TO 80
6     Y=-D4/T+SK1*(EM*W-CK1*S1)+SK2*(8.*D1*D3+6.*D2**2.)+SK2*CK2*W*(2.
1*D3/3.+D1/15.-3.*D5/5.)+SK3*EM*(4.*(D1+D3)+6.*D2+D0)+SK3*CK3*(-4.
2*(D1+D3)+6.*D2+D0+S1)
      GO TO 80
7     Y=-D5/T+SK1*(EM*W-CK1*S1)+10.*(D1*D4+2.*D2*D3)*SK2+SK2*CK2*W*(-D2
1/6.+5.*D4/6.-2.*D6/3.)+SK3*EM*(5.*(D1+D4)+10.*(D2+D3)+D0)+SK3*CK3
2*(5.*(D1+D4)+10.*(D2+D3)+D0+S1)
      GO TO 80
888  TYPE 99,D6,S
99   FORMAT(10A,'D6=',E15.8,5X,'S1=',E15.8)
80   RETURN
      END
C *****
C     FUNCTION A CALCULATES ALPHA
C *****
      FUNCTION A(D0,D1,D2)
      A=-1.+(D1**2)/(D0*D2-D1**2)
      RETURN
      END
C *****
C     FUNCTION G(XB)
C *****
      CALL GAMA(XB,GB,IJ)
      G=GB
      RETURN
      END
C     TO CALCULATE C3A,C4A,C5A
C     SUBROUTINE CF345(G1,G2,G3,G4,G5,F,C3,C4,C5,G6)
C *****
      DIMENSION P(20),E(20)

```

```

DO 10 I=1,12
BBX=I
E(1)=G(BBX)
B=F+I.
10 P(1)=G(B)
T32=3.*P(1)*G1/P(2)
T33=3.*P(1)*G2/P(3)
T34=P(1)*G3/P(4)
C3=1-T32+T33-T34
C *****
T42=T32*4./3.
T43=T33*2.
T44=T34*4.
T45=P(1)*G4/P(5)
C4=1-T42+T43-T44+T45
C *****
T52=T32*5./3.
T53=T33*10./3.
T54=T34*10.
T55=T45*5.
T56=P(1)*G5/P(6)
C5=1-T52+T53-T54+T55-T56
C *****
T1=P(7)/P(1)
T2=P(4)*P(7)/(E(4)*P(1)*E(1))
T3=P(4)*P(8)/(E(3)*P(2)*E(2))
T4=P(4)*P(9)/(E(2)*P(3)*E(3))
T5=P(4)*P(10)/(E(1)*P(4)*E(4))
T6=P(5)*P(7)/(E(5)*P(1)*E(1))
T7=P(5)*P(8)/(E(4)*P(2)*E(2))
T8=P(5)*P(9)/(E(3)*P(3)*E(3))
T9=P(5)*P(10)/(E(2)*P(4)*E(4))
T10=P(5)*P(11)/(E(1)*P(5)*E(5))
T11=P(6)*P(7)/(E(6)*P(1)*E(1))
T12=P(6)*P(8)/(E(5)*P(2)*E(2))
T13=P(6)*P(9)/(E(4)*P(3)*E(3))
T14=P(6)*P(10)/(E(3)*P(4)*E(4))
T15=P(6)*P(11)/(E(2)*P(5)*E(5))
T16=P(6)*P(12)/(E(1)*P(6)*E(6))
TT1=C3*(T2-T3+T4-T5)
TT2=C4*(T6-T7+T8-T9+T10)
TT3=C5*(T11-T12+T13-T14+T15-T16)
G6=T1+(1./P(1))*(TT1+TT2+TT3)
RETURN
END
C *****
C THIS SUBROUTINE GIVES THE VALUE OF LAMDA6,S1 WITH LAMDAS 0 TO 5 AS
C INPUT
C *****
SUBROUTINE DS61(D0,D1,D2,D3,D4,D5,D6,S)
DIMENSION Y(50)
REAL LX3,LX4,LX5
F=A(D0,D1,D2)
C F STANDS FOR ALPHA
GX0=1.0

```

```

X=XX
ERR=1.0E-6
GX=1.0
10 IF(X-2.0) 50,50,15
15 IF(X-2.0) 110,110,15
X=X-1.0
GX=GX*X
GO TO 10
50 IF(X-1.0) 60,120,110
60 IF(X-ERR) 62,62,80
62 Y=FLOAT(INT(X))-X
IF(ABS(Y)-ERR) 130,130,64
64 IF(1.0-Y-ERR) 130,130,70
70 IF(X-1.0) 80,80,110
80 GX=GX/X
X=X+1.0
GO TO 70
110 Y=X-1.0
GY=1.0+Y*(-0.5771017+Y*(+0.985854+Y*(-0.8764218+Y*(0.8328212+
1 Y*(-0.5684729+Y*(+0.2548205+Y*(-0.05149930))))))
GX=GX*GY
120 RETURN
130 IER=1
RETURN
END

```